

Simulação Computacional dos Materiais

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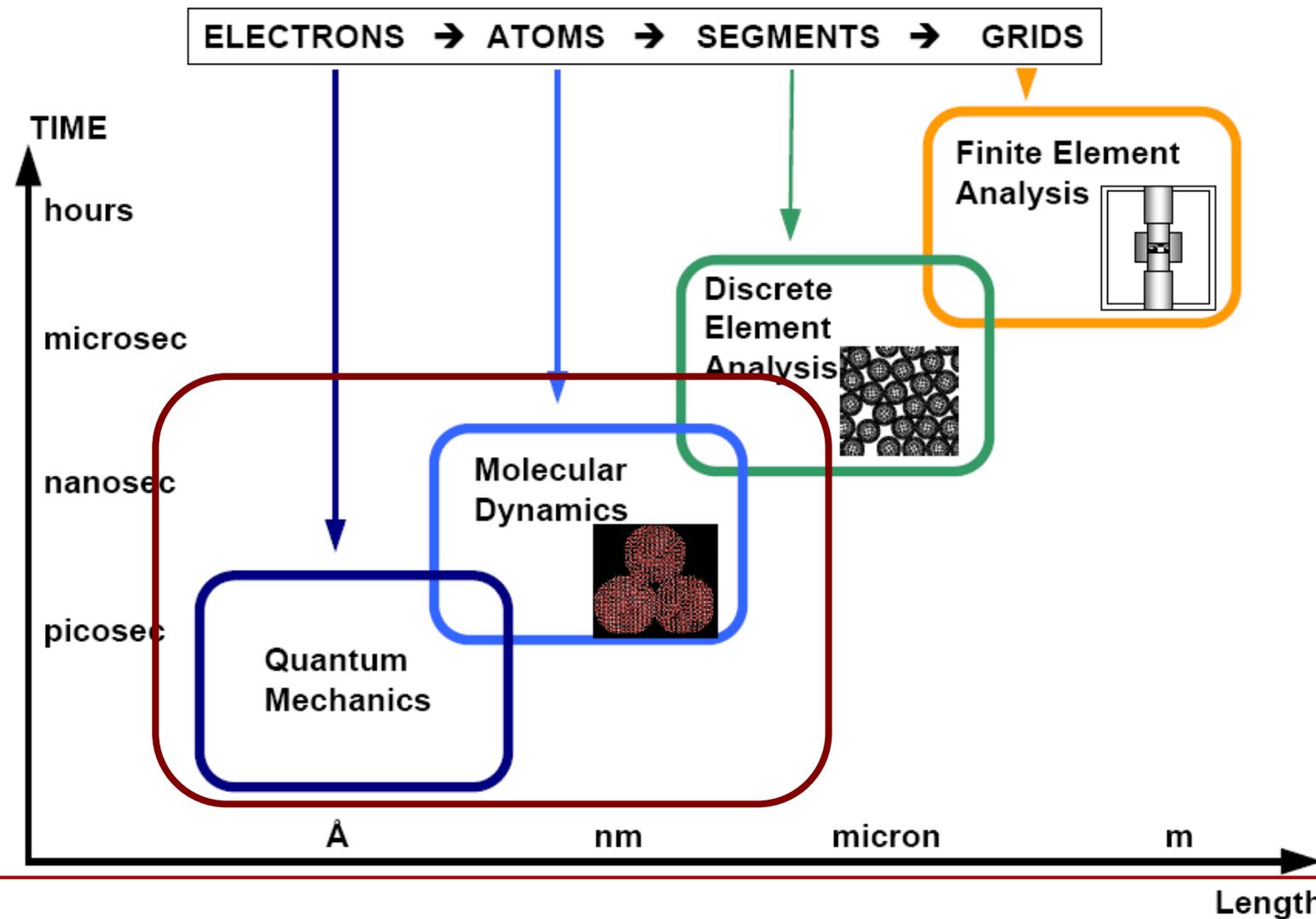
AULA 9 – 17/09/2020

Parte A



Introdução

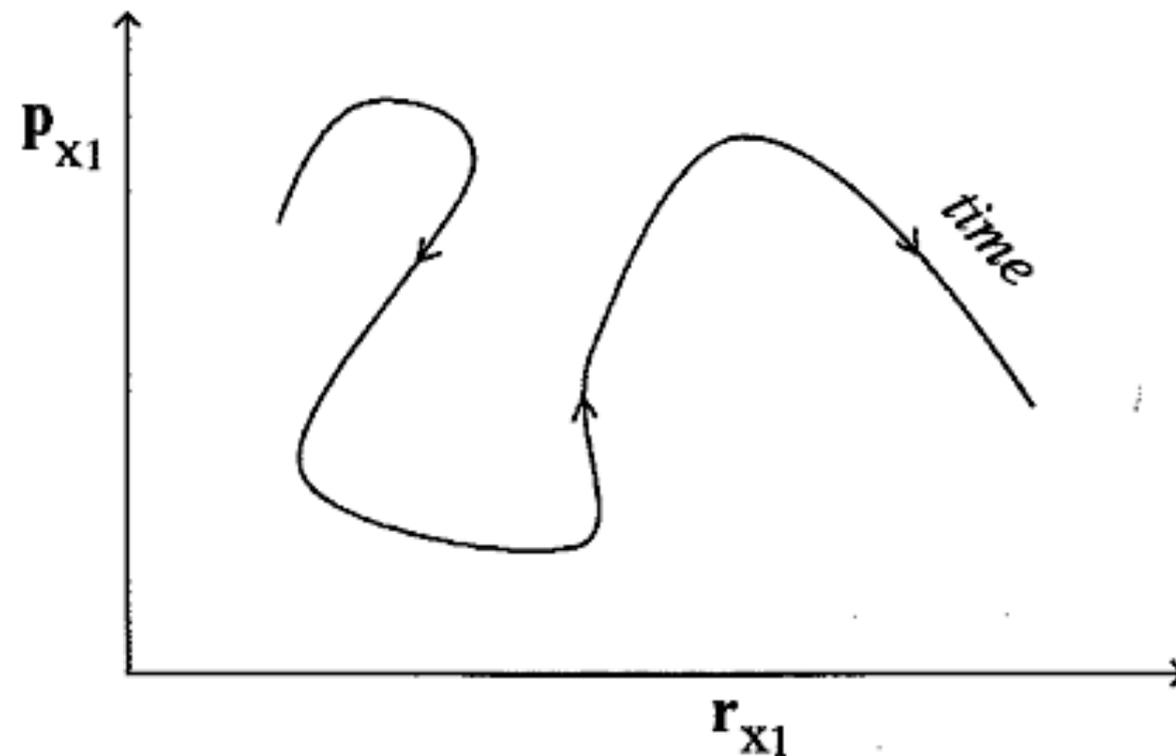
Multi-scale Computational Hierarchy of Materials Simulations



De volta para o futuro

Simulações moleculares provem um maneira de:

- 1) Calcular as médias temporais de um observável*
- 2) Visitar os pontos mais importantes do espaço de fases.*



Conhecendo o espaço de fases e as médias temporais, podemos conhecer as propriedades MACROscópicas do sistema.

Figure 5.1: Motion of a point in a two-dimensional phase space. The diagram only maps the temporal evolution of two coordinates, $r_{x_1}(t)$ and $p_{x_1}(t)$, out of the $6N$ coordinates, $r_{x_1}(t), r_{x_2}(t), \dots, r_{x_N}(t), p_{x_1}(t), p_{x_2}(t), \dots, p_{x_N}(t)$. The arrows indicate the continuous increase of time.

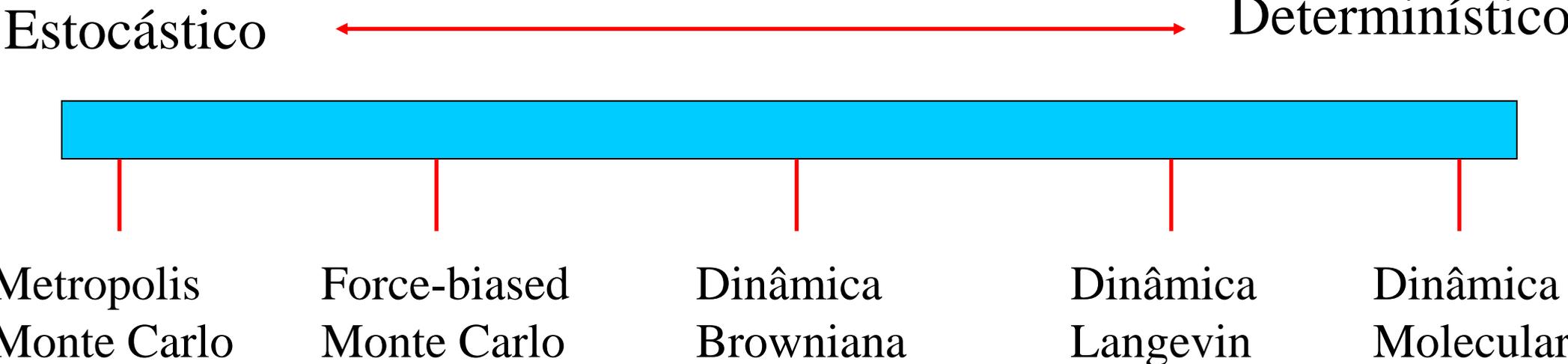
O Slide mais importante da parte I

Média do Ensemble = Média temporal

$$\langle \mathbf{A} \rangle_{\text{NVT}} = \lim_{t_{\text{sim}} \rightarrow \infty} \frac{1}{t_{\text{sim}}} \int_{t_0}^{t_0 + t_{\text{sim}}} \mathbf{A}(\tau) d\tau$$



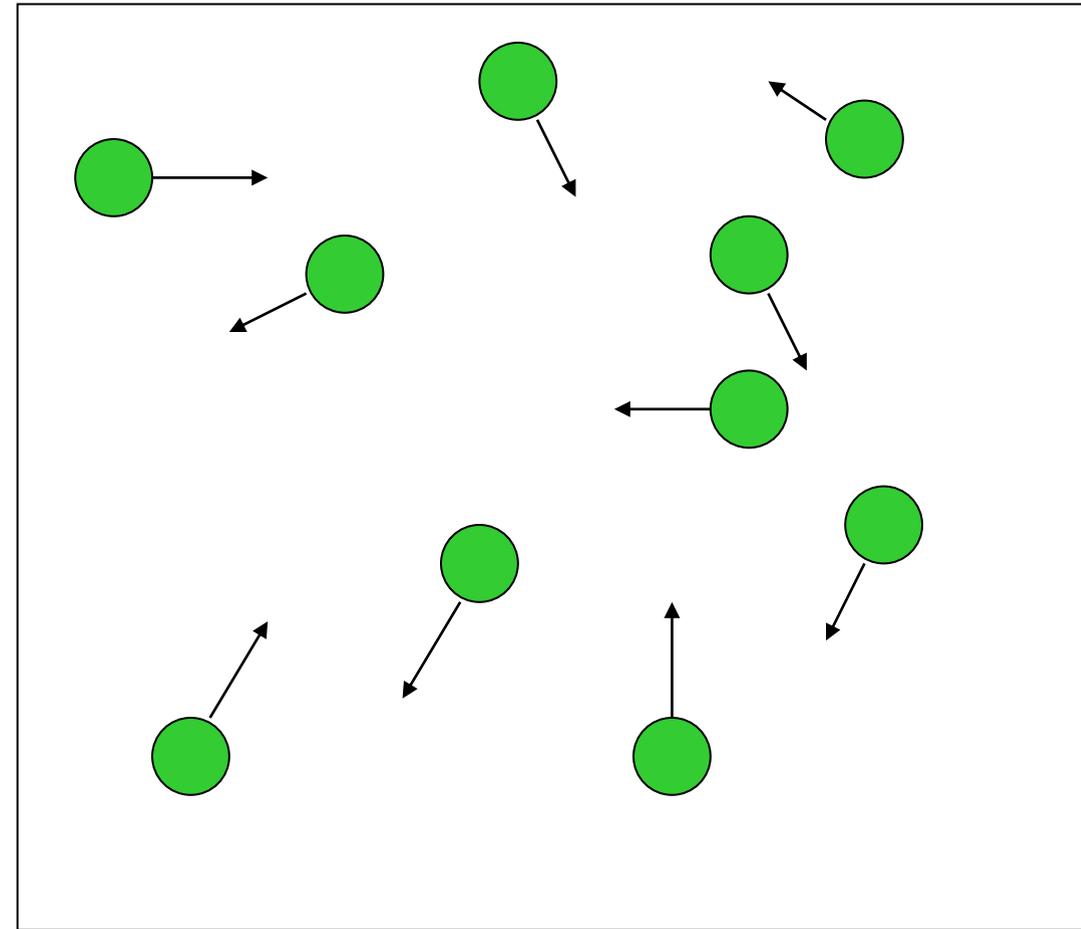
Estocástico x Determinístico



Dinâmica Molecular

Equações de movimento de Newton

$$m \frac{d^2 \vec{r}_i}{dt^2} = -\nabla_i V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$$



Dinâmica Molecular

As propriedades podem ser obtidas por amostragem do sistema a um dado ensemble (NPT, NVT, NVE, gran-canonical, ...)

$$\langle \mathbf{A} \rangle_{\text{NVT}} = \int d\Gamma \rho_{\text{NVT}} \mathbf{A}(\Gamma)$$
$$\rho_{\text{NVT}}(\Gamma) = \frac{e^{-\beta \mathcal{H}(\Gamma)}}{Z_{\text{NVT}}}$$

where

$$\left\{ \begin{array}{l} \beta = \frac{1}{k_B T} \\ \mathcal{H} = K + V \\ Z_{\text{NVT}} = \int d\Gamma \rho_{\text{NVT}} \end{array} \right.$$

Hipótese
Ergódica

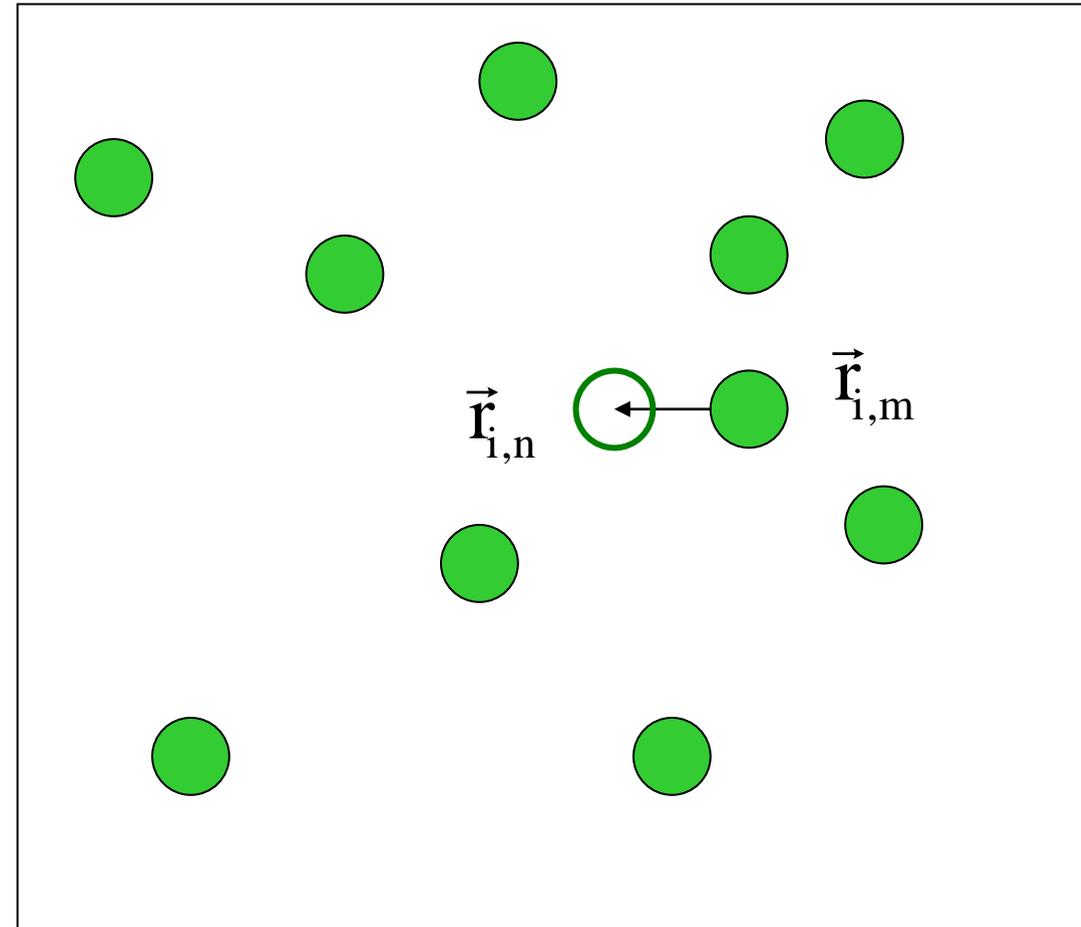
$$\langle \mathbf{A} \rangle_{\text{NVT}} = \lim_{t_{\text{sim}} \rightarrow \infty} \frac{1}{t_{\text{sim}}} \int_{t_0}^{t_0 + t_{\text{sim}}} \mathbf{A}(\tau) d\tau$$

Monte Carlo

Probabilidade
de transição:

$$\frac{\rho_n}{\rho_m} = \frac{Z^{-1}_{NVT} e^{-\beta V_n}}{Z^{-1}_{NVT} e^{-\beta V_m}} = e^{-\beta \Delta V_{nm}}$$

onde $\Delta V_{nm} = V_n - V_m$



Monte Carlo

Algoritmo de Metropolis

$$\Delta V_{nm} > 0$$

$$\text{Ranf} < e^{-\beta \Delta V_{nm}} \text{ aceita}$$

$$\text{Ranf} \geq e^{-\beta \Delta V_{nm}} \text{ rejeita}$$

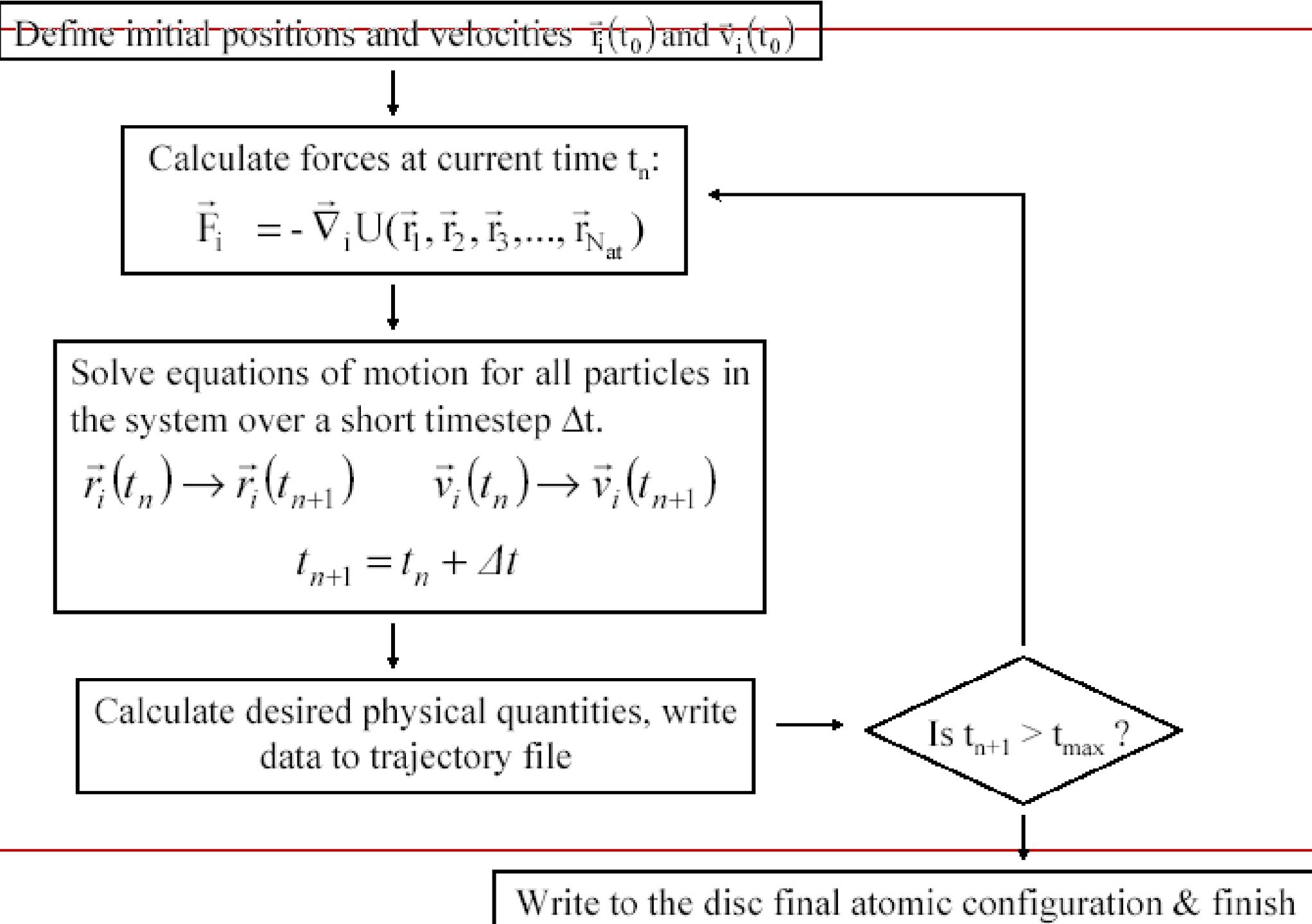
onde Ranf é um número randômico entre [0,1]

$$\Delta V_{nm} \leq 0$$

$$e^{-\beta \Delta V_{nm}} \geq 1 \text{ aceita}$$

$$\langle A \rangle_{NVT} = \lim_{N_{\text{steps}} \rightarrow \infty} \frac{1}{N_{\text{steps}}} \sum_{\tau=1}^{N_{\text{steps}}} A(\tau)$$

Schematic diagram of a basic MD code



Interações interatômicas

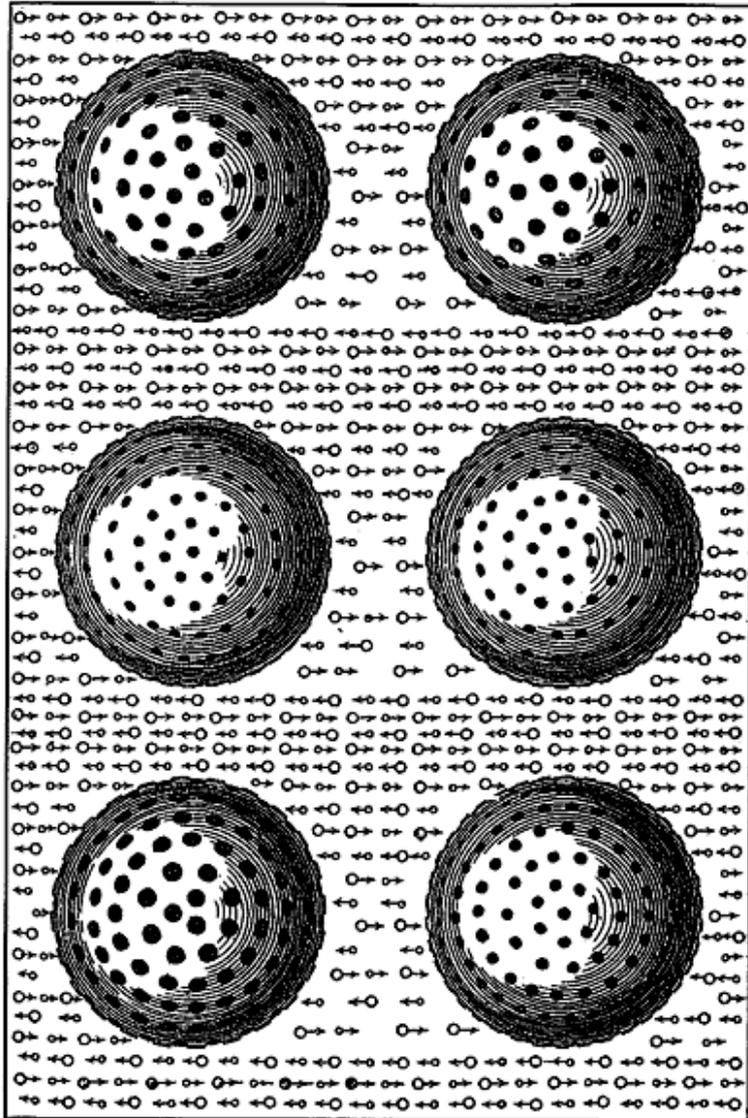
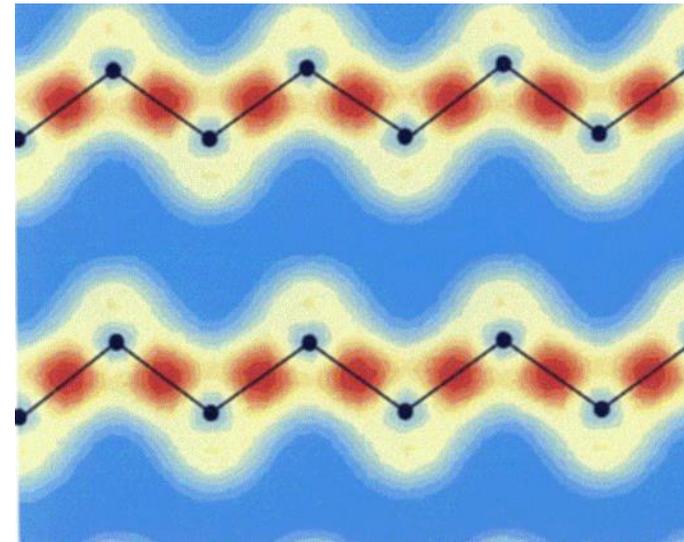
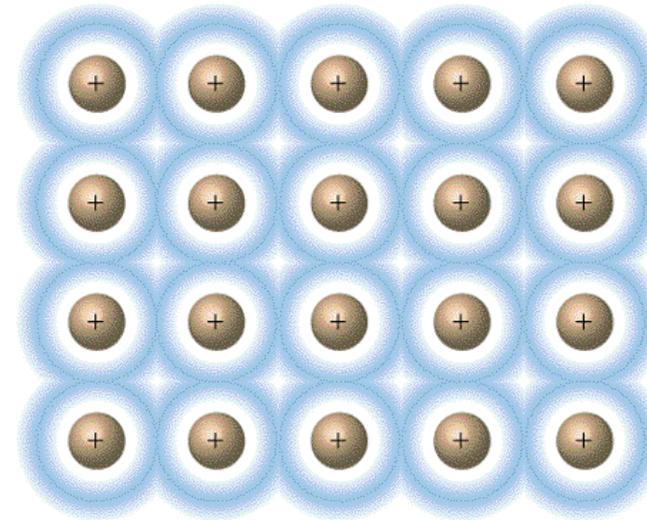


Fig. 2.2 Le Sage's picture of attraction between particles of matter [249].

Corpuscules ultramondains



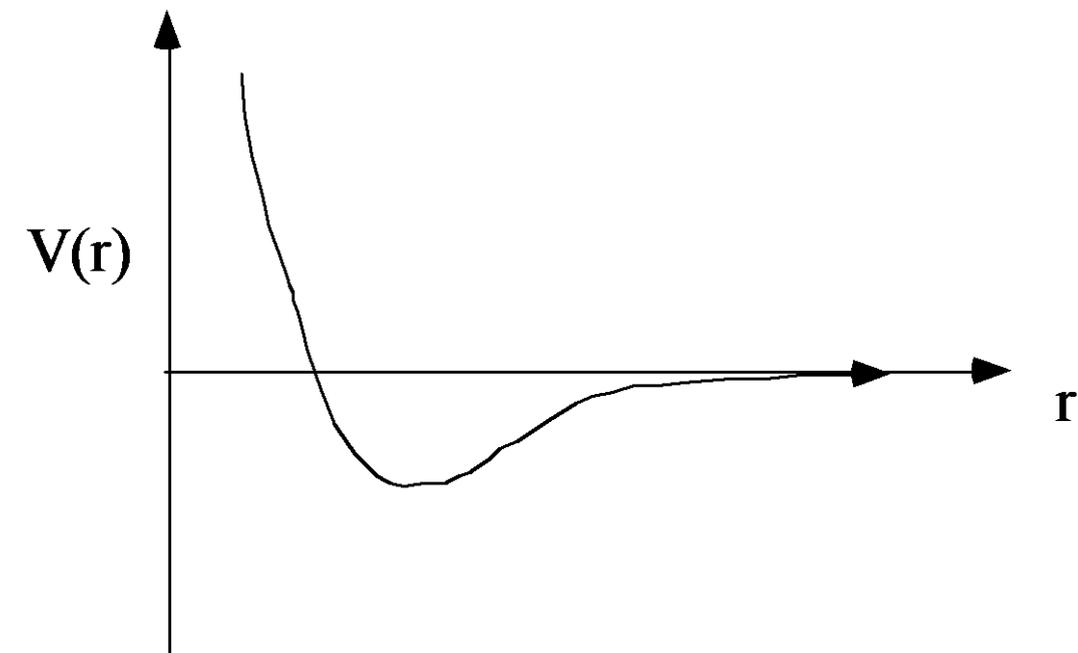
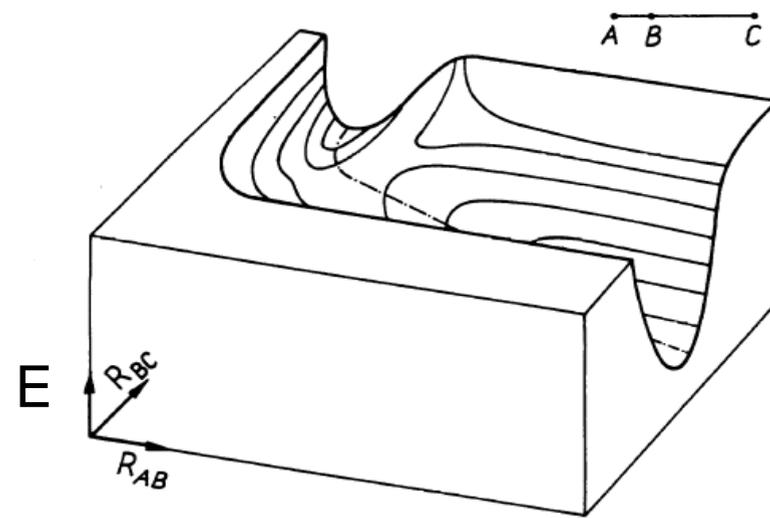
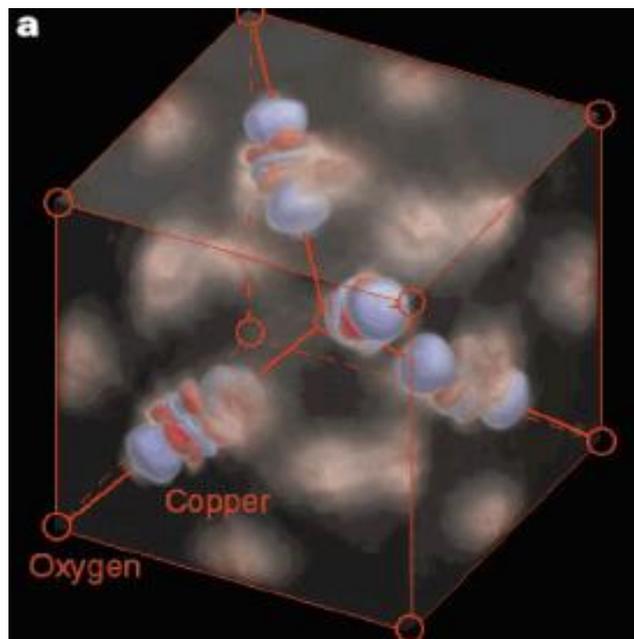
O que a simulação atomística envolve?

Modelagem de materiais em escala atômica.

LIGAÇÃO pode ser descrita como:

Mecânica Quântica: calcula a energia total em função da estrutura.

Potenciais efetivos (funções analíticas que descrevem aproximadamente como a energia varia em função da distância interatômica ou geometria)



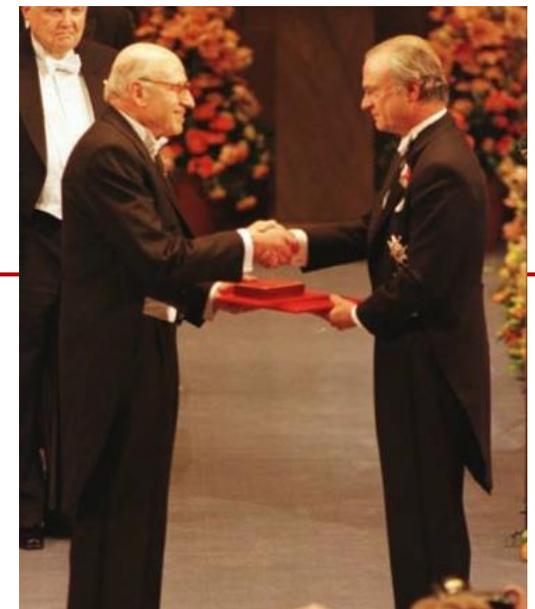
Cálculos de primeiros princípios

Resolve numericamente a equação de Schrödinger

Teoria do Funcional da Densidade (DFT)

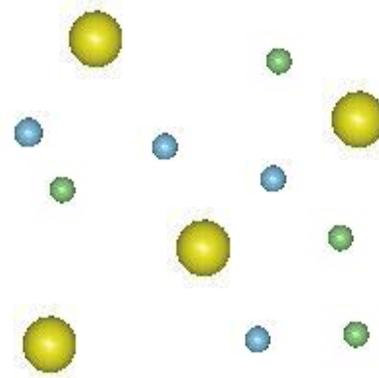
Pseudopotenciais

Quantum-Espresso, SIESTA, VASP and Gaussian



Kohn - Nobel Prize 99

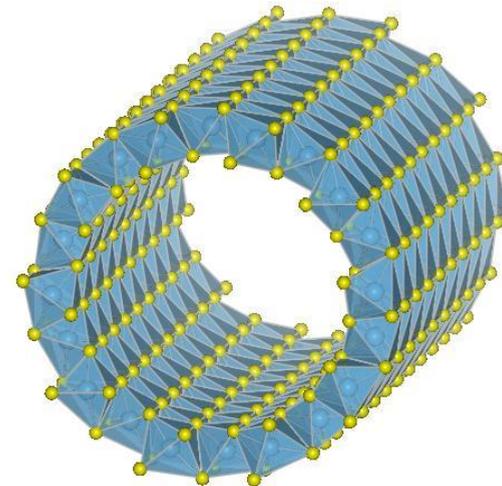
Composição



$$H\psi = E\psi$$



Estruturas



Propriedades

Termodinâmica

Parâmetro de rede

Constante elástica

Estrutura eletrônica

Cinética

Aproximação de Born Oppenheimer

Átomos I são caracterizados pelo vetor coordenada \vec{R}_i

Sistema caracterizado pela função de onda ψ

Born Oppenheimer

$$E(\vec{R}_i) = \min_{\psi} E(\vec{R}_i, \psi)$$

Para todo conjunto de coordenadas eletrônicas R_i estão no estado fundamental

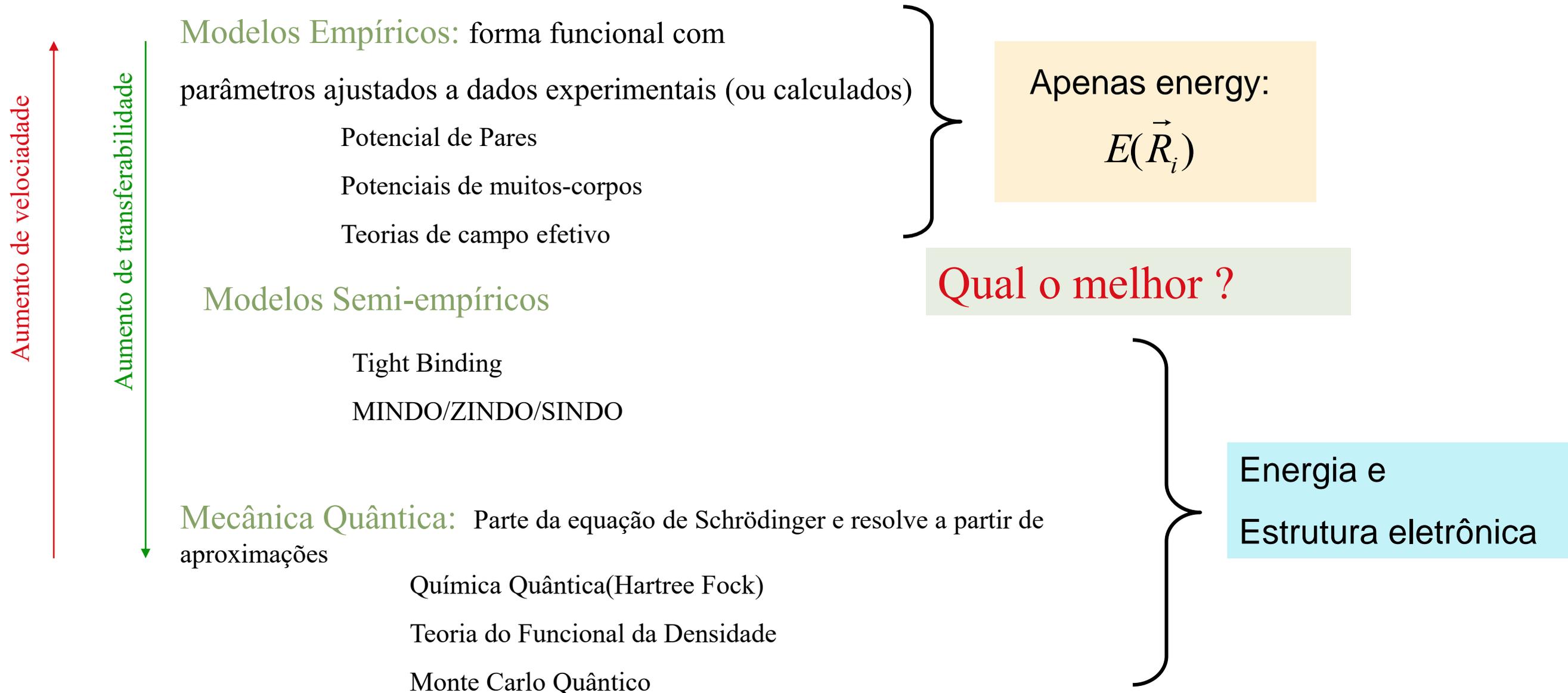
Limites da aplicação da BO

Temperatura

Longas excitações

Modelos de energia

Importante porque é a representação da química/material



Feynman's view point

AUGUST 15, 1939

PHYSICAL REVIEW

VOLUME 56

Forces in Molecules

R. P. FEYNMAN

Massachusetts Institute of Technology, Cambridge, Massachusetts

(Received June 22, 1939)

Formulas have been developed to calculate the forces in a molecular system directly, rather than indirectly through the agency of energy. This permits an independent calculation of the slope of the curves of energy *vs.* position of the nuclei, and may thus increase the accuracy, or decrease the labor involved in the calculation of these curves. The force on a nucleus in an atomic system is shown to be just the classical electrostatic force that would be exerted on this nucleus by other nuclei and by the electrons' charge distribution. Qualitative implications of this are discussed.



Once the spatial distribution of the electrons has been determined by solving the **Schrödinger equation**, all the forces in the system can be calculated using **classical electrostatics**.

The Hellmann-Feynman theorem

It states that for any perturbation λ , the first derivative of the ground state energy of the Hamiltonian H , can be calculated by using the variational property of the wave function ψ_λ

$$\hat{H}_\lambda |\psi_\lambda\rangle = E_\lambda |\psi_\lambda\rangle \quad \langle \psi_\lambda | \psi_\lambda \rangle = 1$$

$$\frac{dE_\lambda}{d\lambda} = \left\langle \psi_\lambda \left| \frac{d\hat{H}_\lambda}{d\lambda} \right| \psi_\lambda \right\rangle$$

Luke, use massa vezes a
aceleração! ou o teorema de
Hellmann - Feynman

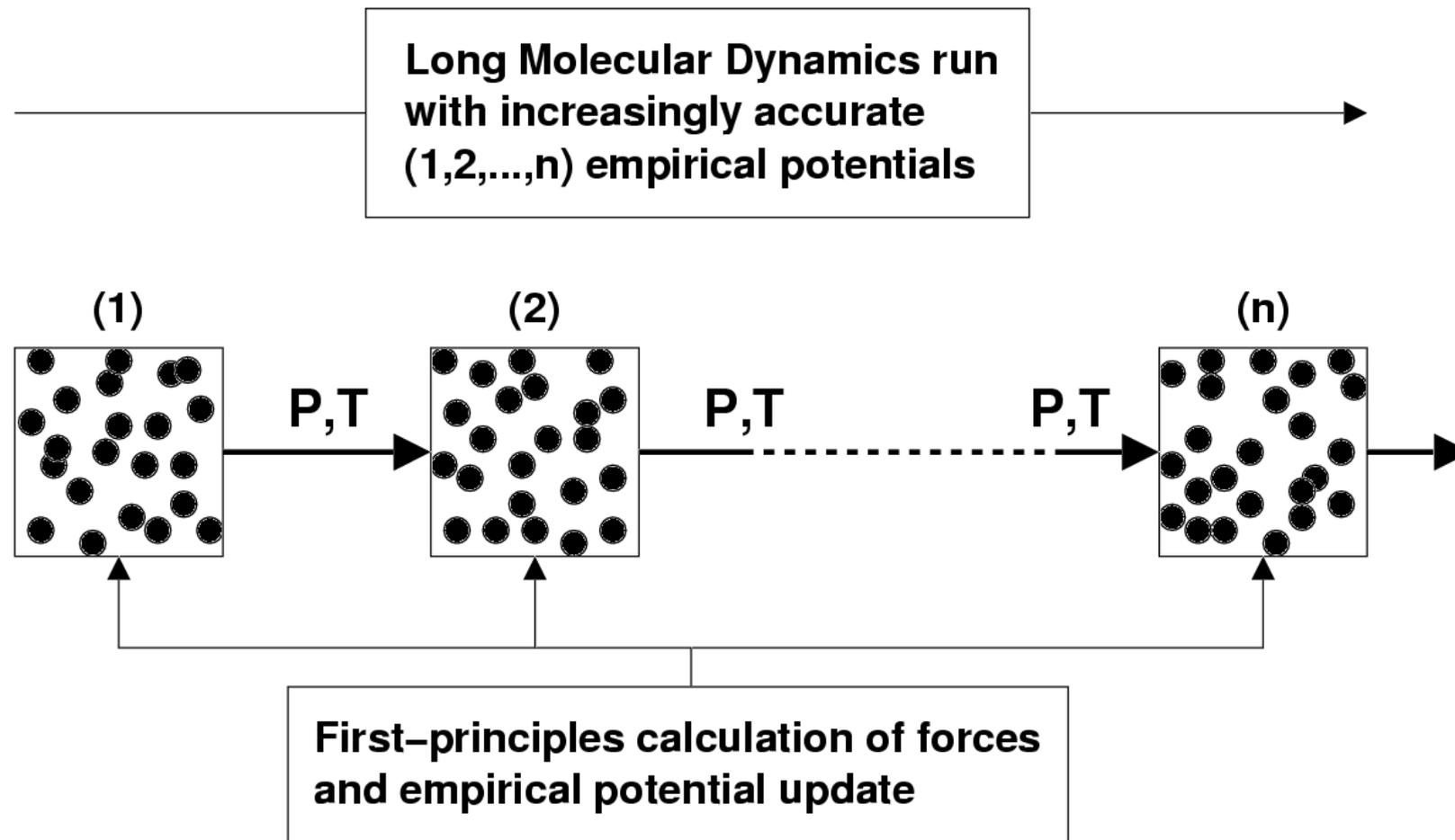


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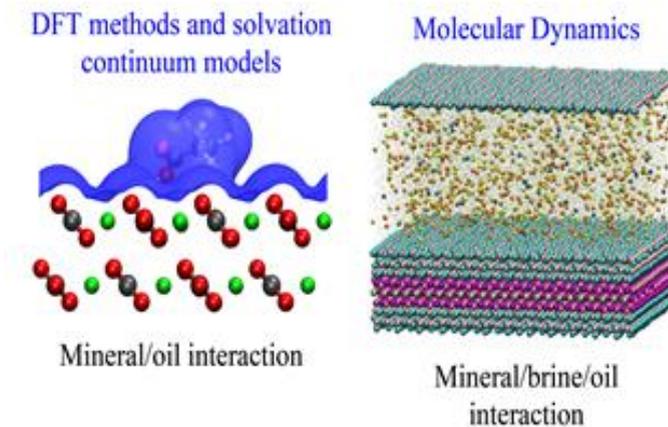
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Do quântico ao atômico



- Assumption: DFT+vdW accuracy is OK
- Effective potential fitted to DFT



**“Optimized”
potential at P,T**

A. Laio et al, Science 287, 1027 (2000)

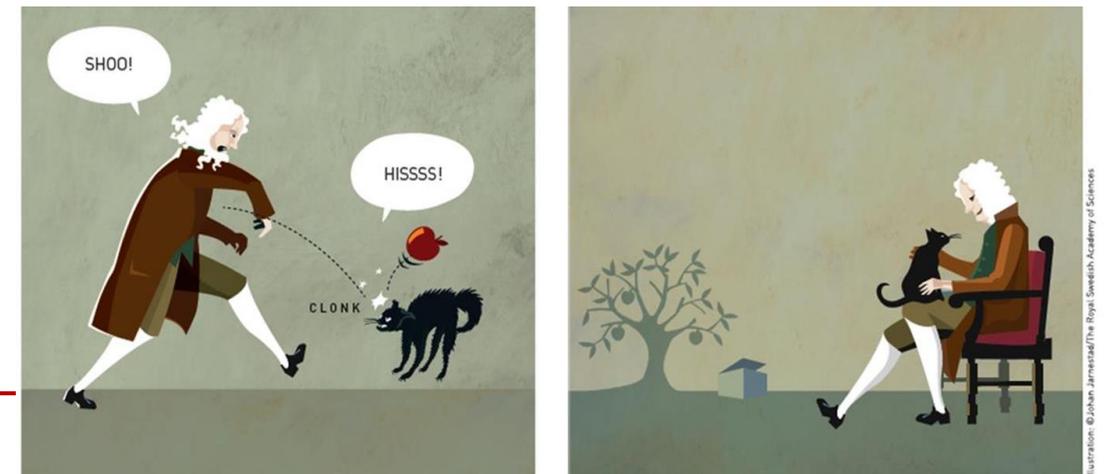
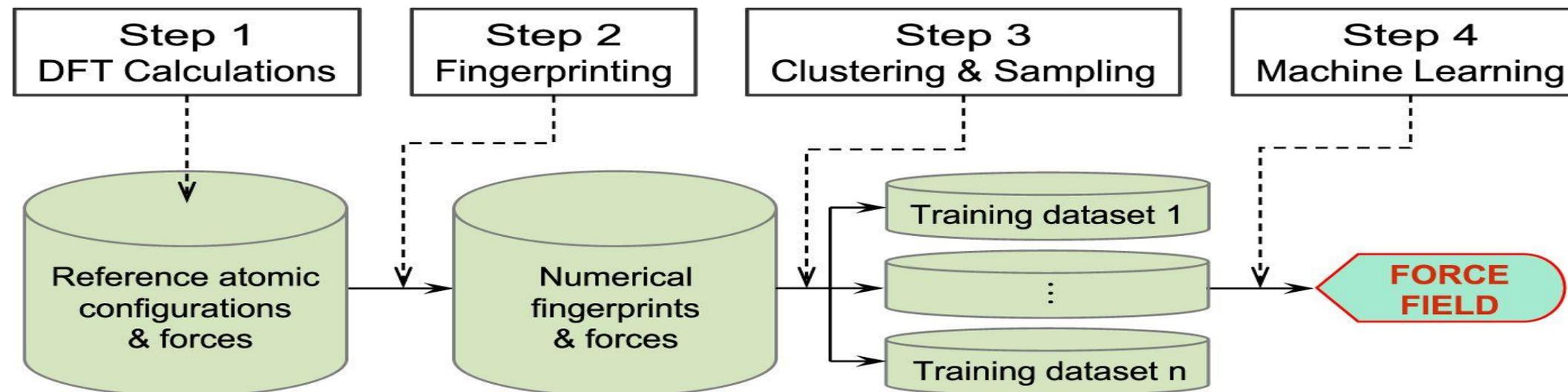
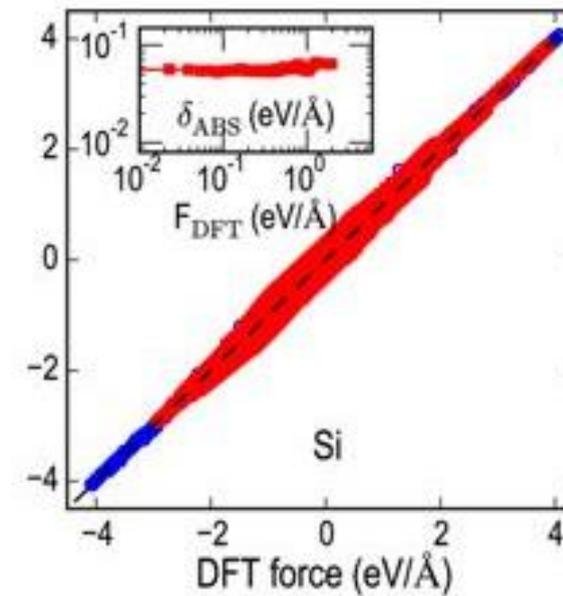
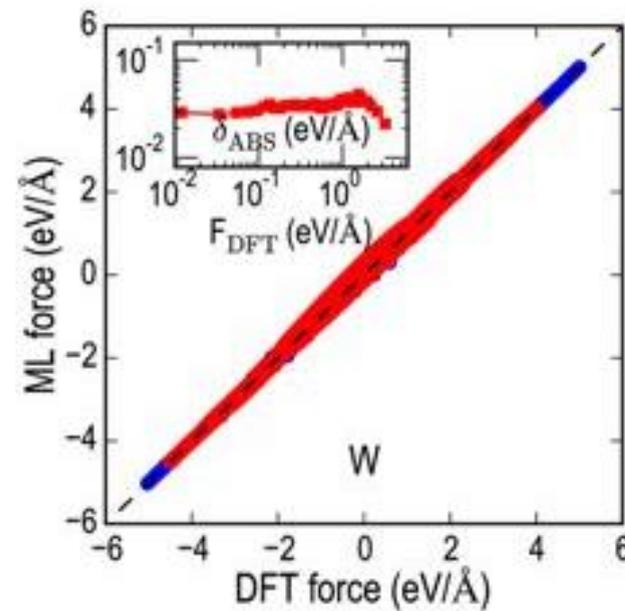
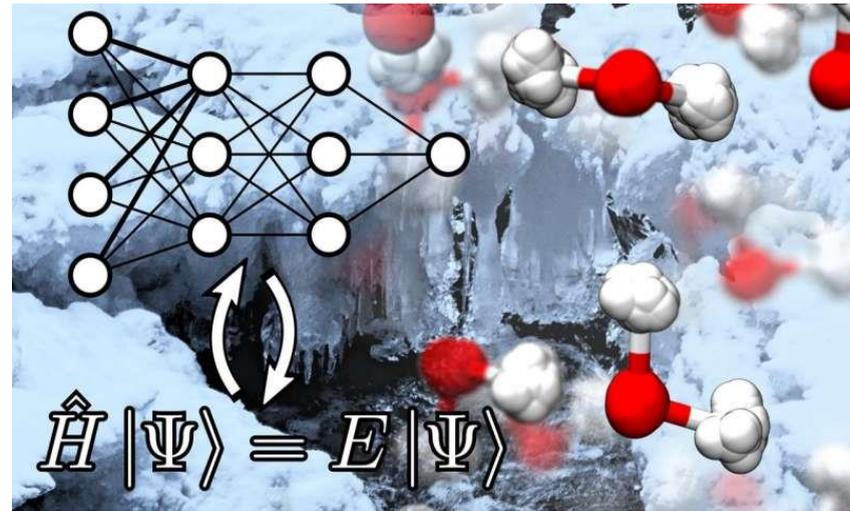


Illustration: ©Johan Jarnestad/The Royal Swedish Academy of Sciences

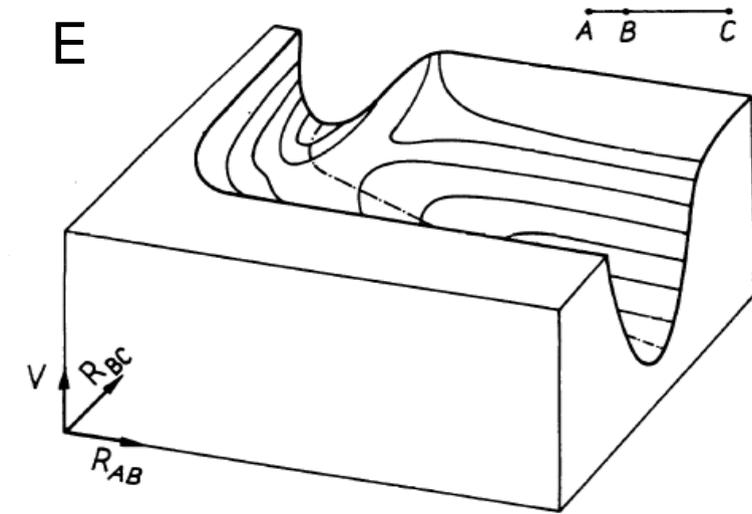
Interatomic potential combining DFT + ML



Limitações da Dinâmica Molecular (I)

1) Descrição clássica da interação interatômica

- Elétrons não estão explicitamente presentes
(Superfície de energia potencial)
- Superfície de energia potencial é aproximada por uma função analítica que fornece a energia potencial U em função das coordenadas.
- Forças são obtidas do gradiente da superfície de energia potencial.



Limitações da Dinâmica Molecular (I)

2) Em Dinâmica Molecular clássica, a eq. de Schrödinger para os núcleos é substituída pela eq. de Newton.

Quão boa é essa aproximação ?

Efeitos quânticos são relevantes quando o comprimento de onda de de Broglie Λ é maior que a distância entre partículas.

$$\lambda_{dB} = \left(\frac{2\pi\hbar^2}{mk_B T} \right)^{1/2}$$

Limitações da Dinâmica Molecular (I)

For the thermal motion we can use the thermal de Broglie wavelength:

$$\Lambda_{th} = \frac{h}{\sqrt{2\pi mk_B T}}$$

For T = 300 K we have

- $\Lambda_{th} = 1 \text{ \AA}$ for a H atom
- $\Lambda_{th} = 0.19 \text{ \AA}$ for a Si atom
- $\Lambda_{th} = 0.16 \text{ \AA}$ for an Ar atom
- $\Lambda_{th} = 0.07 \text{ \AA}$ for a Au atom

Typical interatomic spacing in solid-state materials is $d \sim 1\text{-}3 \text{ \AA}$. Therefore:

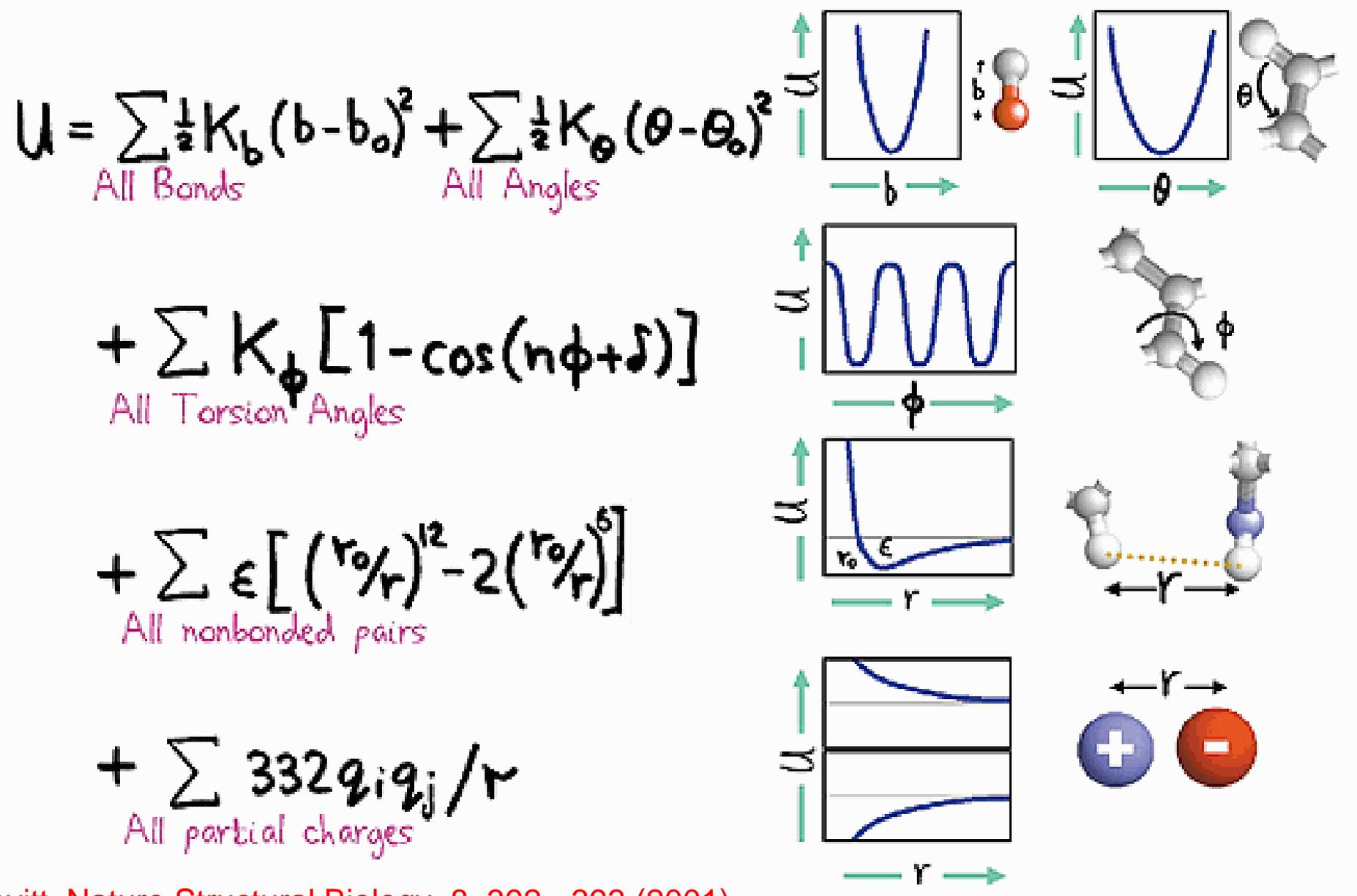
- The wave nature of electron dominates over the particle behavior, electrons can not be considered within classical approximation.
 - All atoms, except for the lightest ones such as H, He, Ne, can be considered as “point” particles at sufficiently high temperature ($d \gg \Lambda$) and classical mechanics can be used to describe their motion.
-

Discussão dos modelos empíricos de energia

- Potenciais de pares: formas e limitações físicas
- Classificação dos modelos empíricos
- Potenciais de muito-corpos
- Funcionais de pares
- Potenciais dependente do ambiente (química)

Objetivo: Noções das formas típicas dos potenciais e entender as limitações das várias escolhas. Foco na forma, não nos parâmetros.

Potenciais para moléculas complexas



Somatório das energias de pares: Potenciais de pares

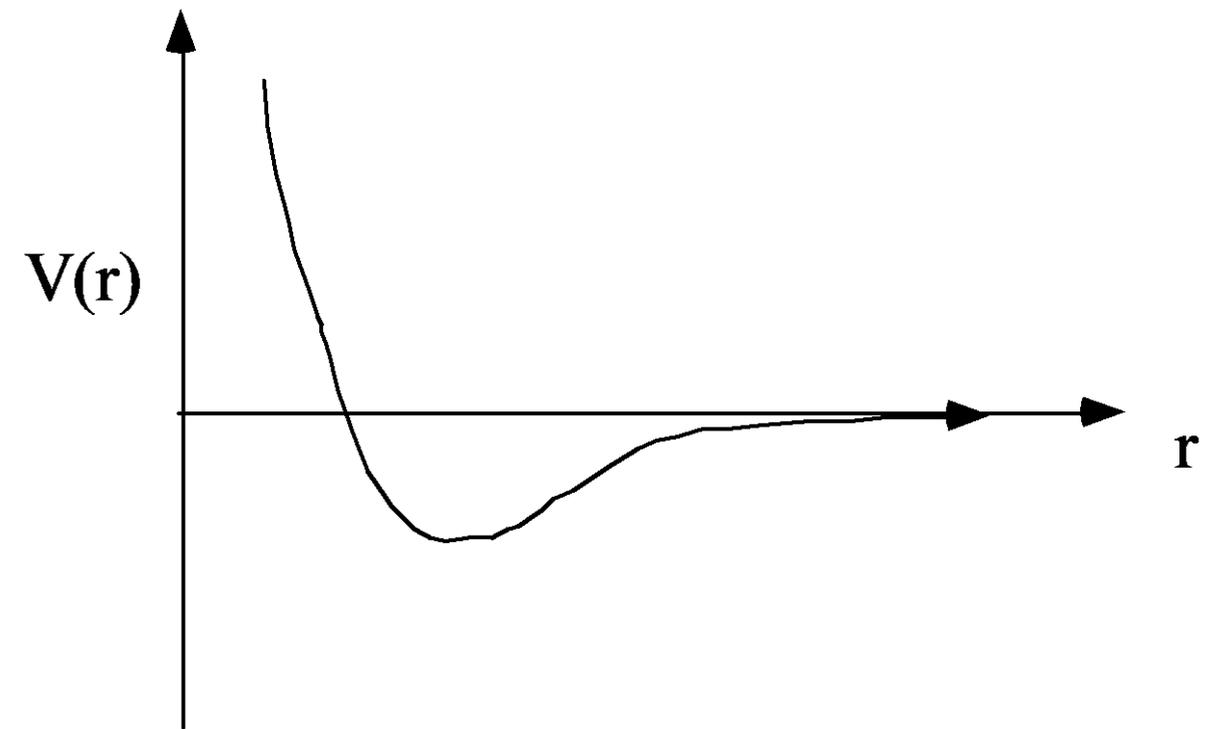
$$E = (E_0) + \frac{1}{2} \sum_{i,j \neq i}^N V(\vec{R}_i - \vec{R}_j)$$

Características comuns:

Repulsivo em distâncias curtas

Atrativo em distâncias intermediárias e longas

Normalmente aplicamos um raio de corte !

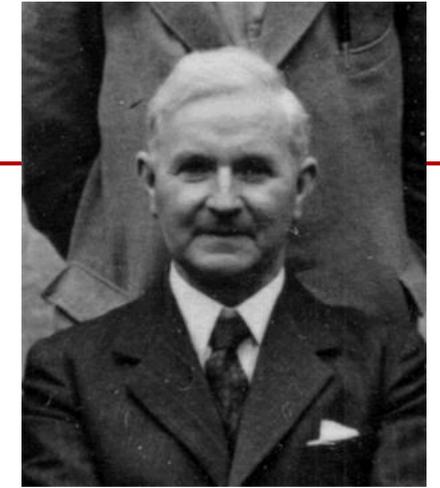


Formas analíticas dos potenciais são baseadas em fundamentos físicos

Relevância física tende a desaparecer quanto as constantes do potencial são ajustadas

Mínimo conjunto de parâmetros: escalas de energia e comprimento

Lennard-Jones: modelo simples com 2 parâmetros



$$V(r) = \frac{A}{r^{12}} - \frac{B}{r^6}$$

$$\frac{V(r)}{\varepsilon} = \left[\left(\frac{\sigma}{r} \right)^{12} - 2 \left(\frac{\sigma}{r} \right)^6 \right]$$

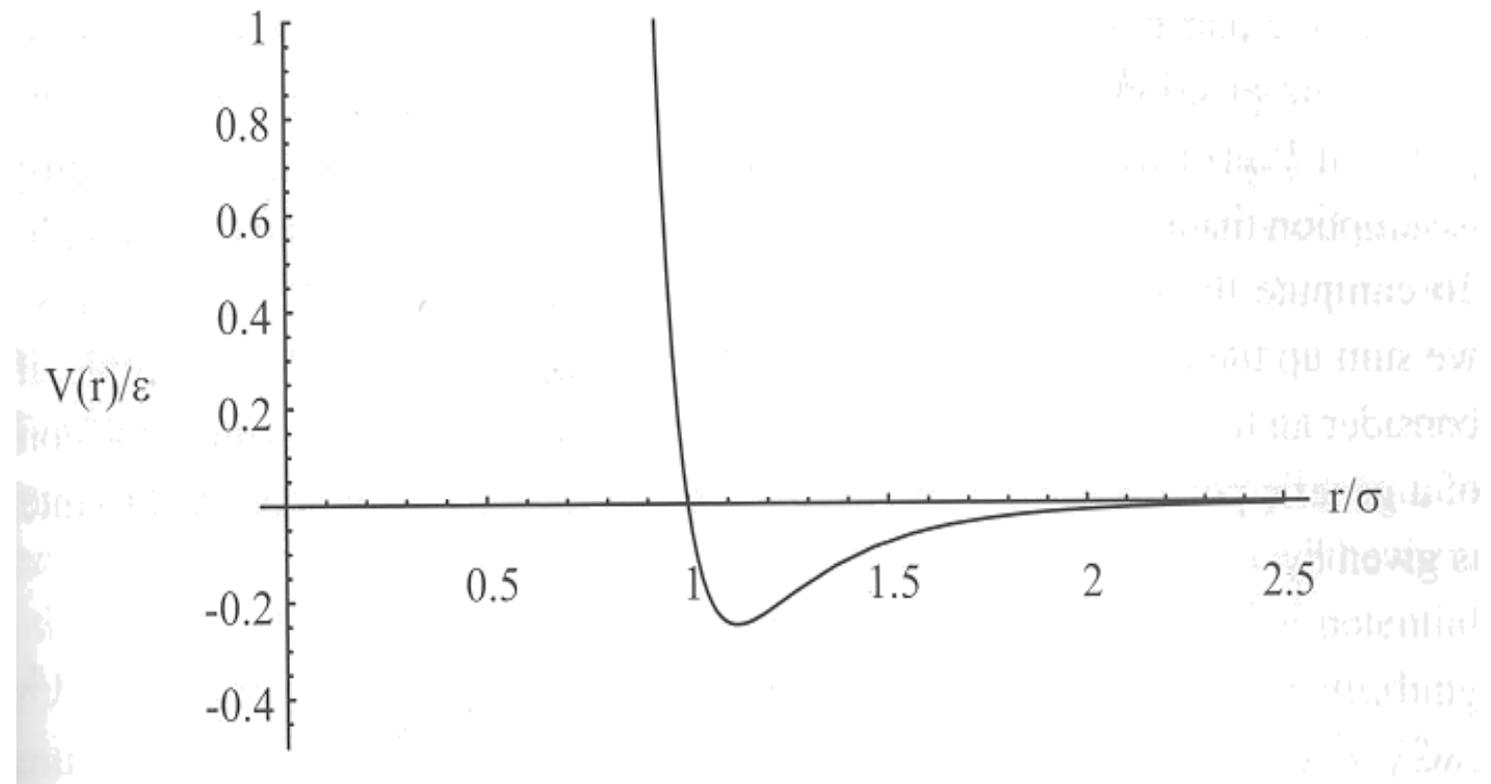
ε define a escala de energia
 σ define a escala de comprimento

Todos os sistemas LJ são idênticos quando escrevemos a temperatura, pressão e densidade em unidades renormalizadas.

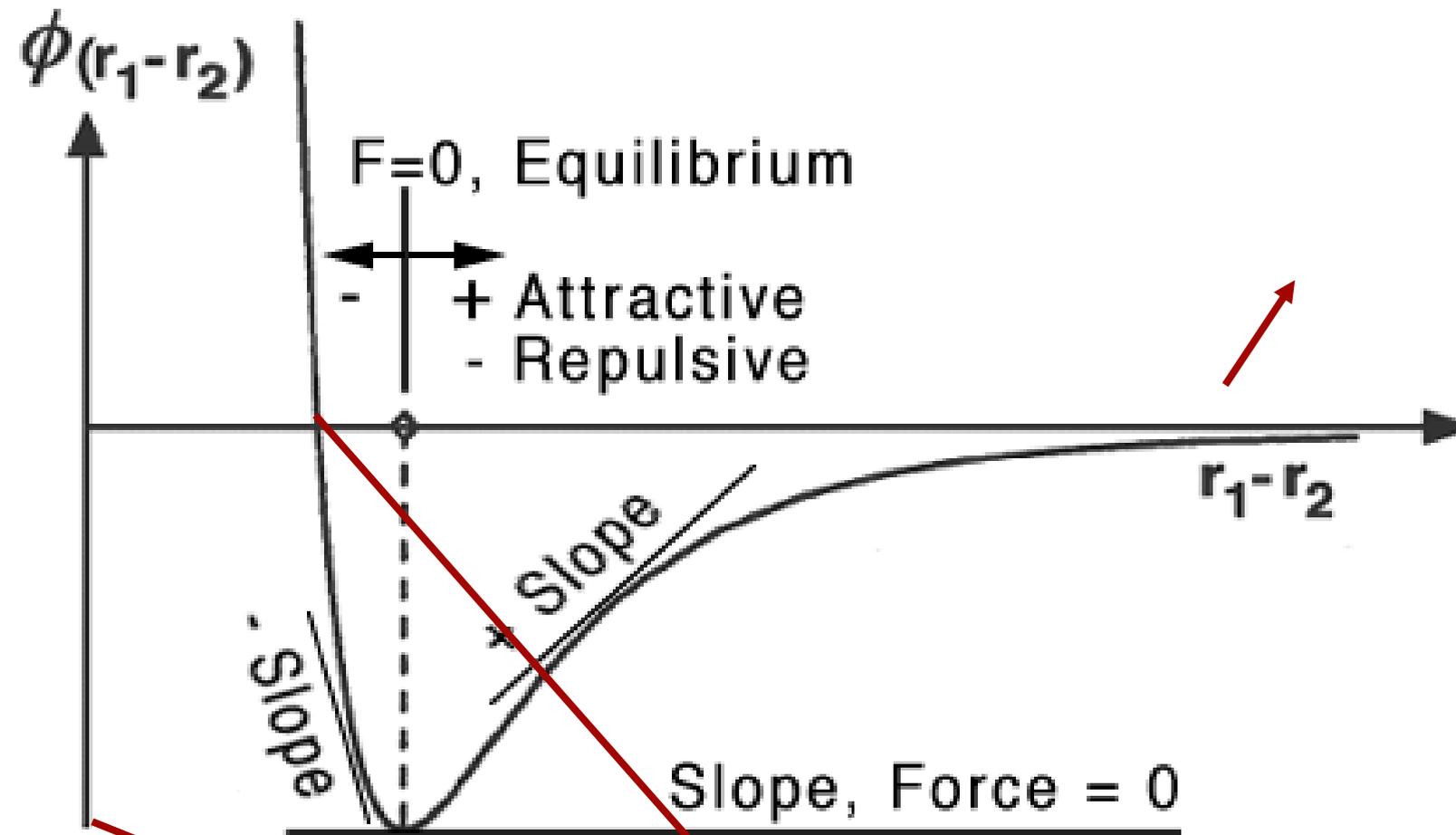
$$\text{Temperature: } \frac{\varepsilon}{k_B}$$

$$\text{Pressure: } \frac{\varepsilon}{\sigma^3}$$

$$\text{Density: } \frac{1}{\sigma^3}$$



Potencial Lennard-Jones



$$u(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

Potencial Lennard-Jones

O Potencial LJ é uma aproximação. A forma do termo de repulsão não tem justificativa teórica.

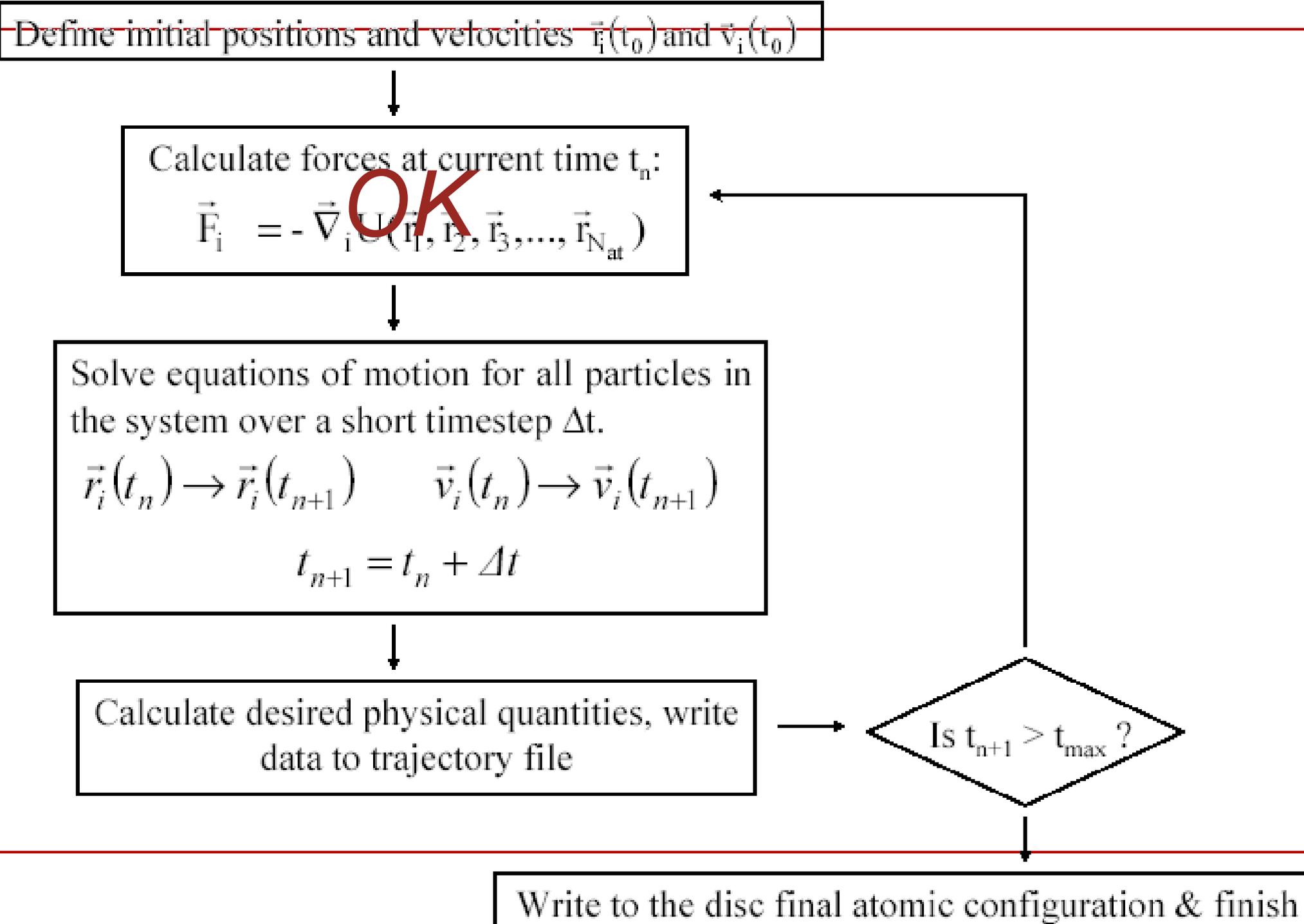
A força de repulsão deve depender **EXPONENCIALMENTE** com a distância,

Mas o termo de repulsão da fórmula de LJ é mais conveniente pela facilidade e eficiência no cálculo do termo

r^{12} sendo o quadrado de r^6 .

O Potencial atrativo de longo alcance, contudo, é derivado das interações de **DISPERSÃO** (London).

Schematic diagram of a basic MD code



Simulação Computacional dos Materiais

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Parte B



Parte 2 - Subrotina Init

O que é necessário ?

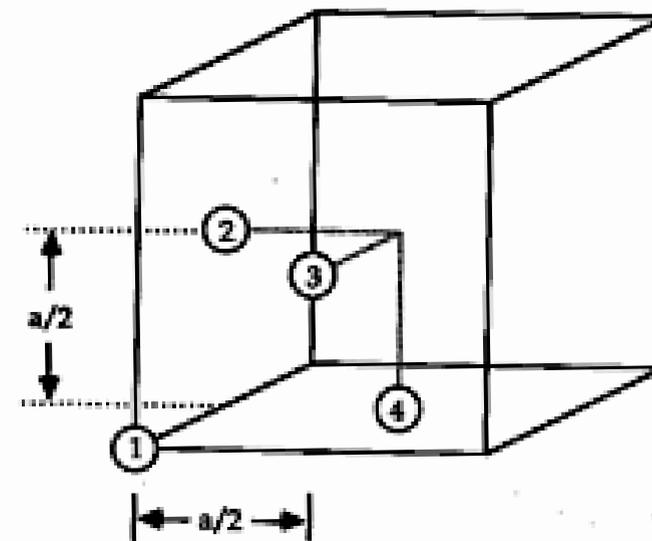
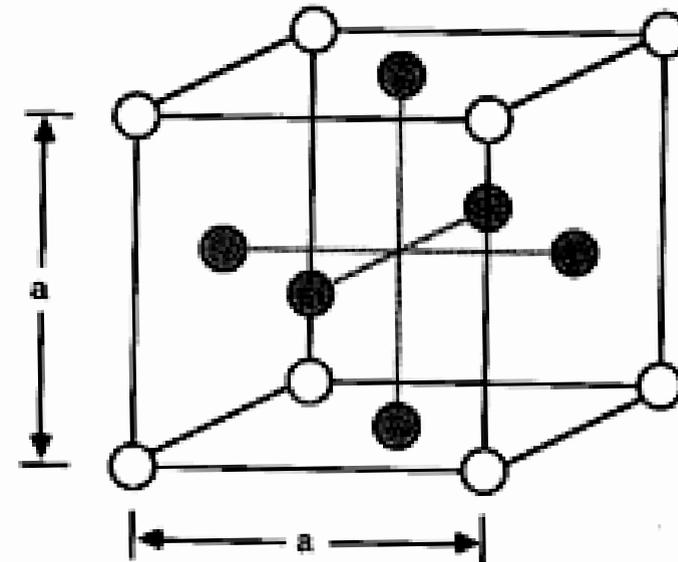
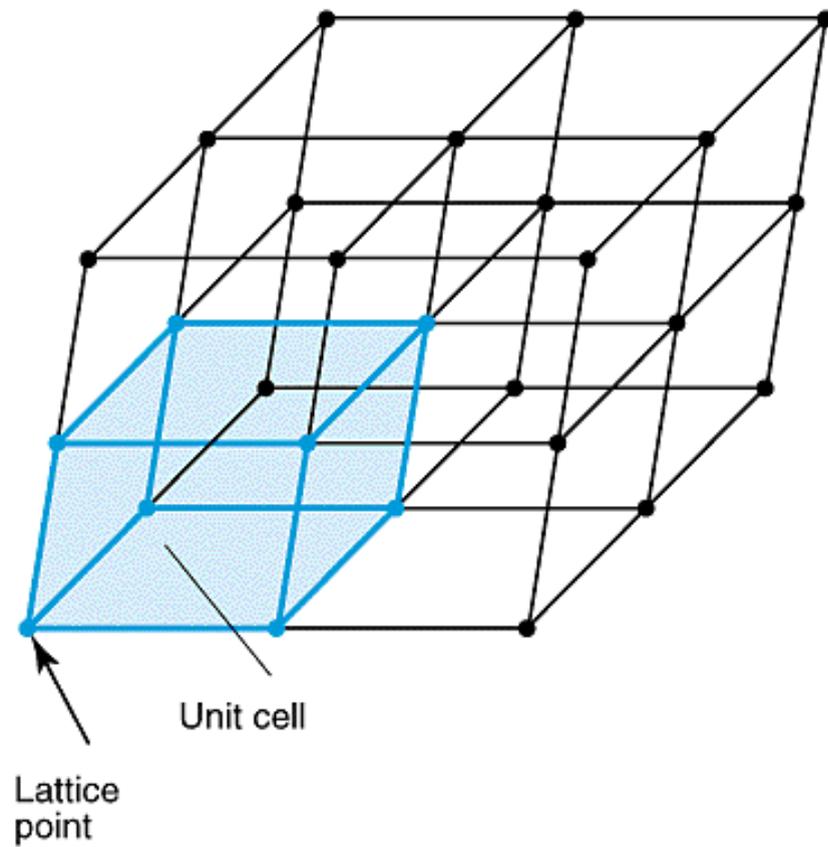
Definir: Condições: Temperatura, volume, número de átomos, ensemble

Coordenadas atômicas: Rede cristalina, minimização da energia, distribuição randômica, informação experimental, ...

Velocidades: Distribuição de Maxwell-Boltzmann das velocidades
Fornece a temperatura média do sistema

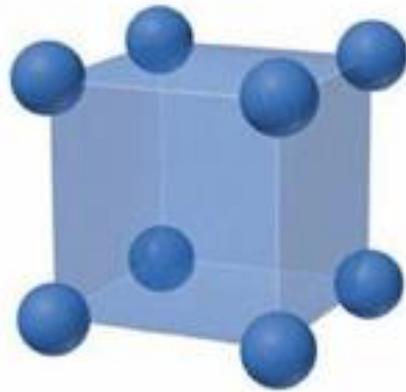
Acelerações: das forças das coordenadas atômicas iniciais

Posições iniciais

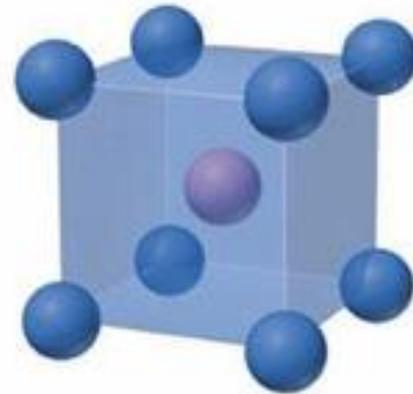


Posições iniciais

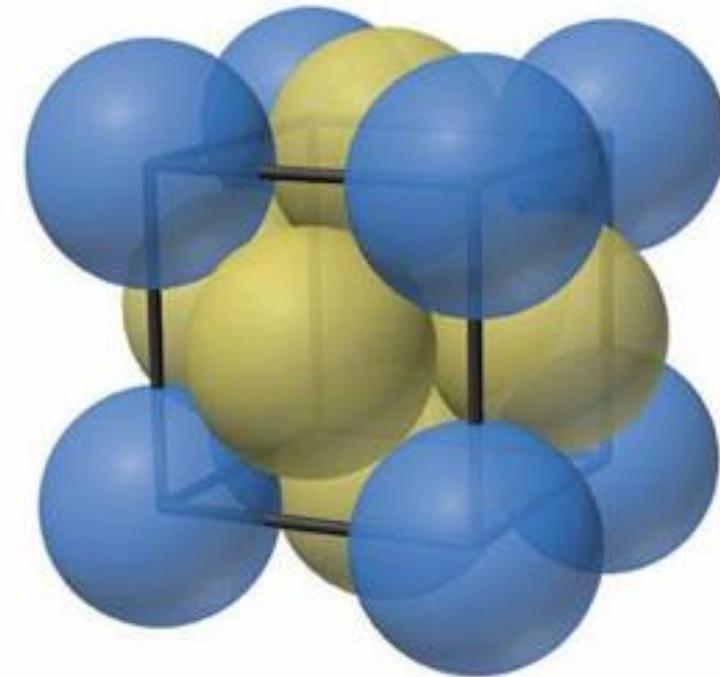
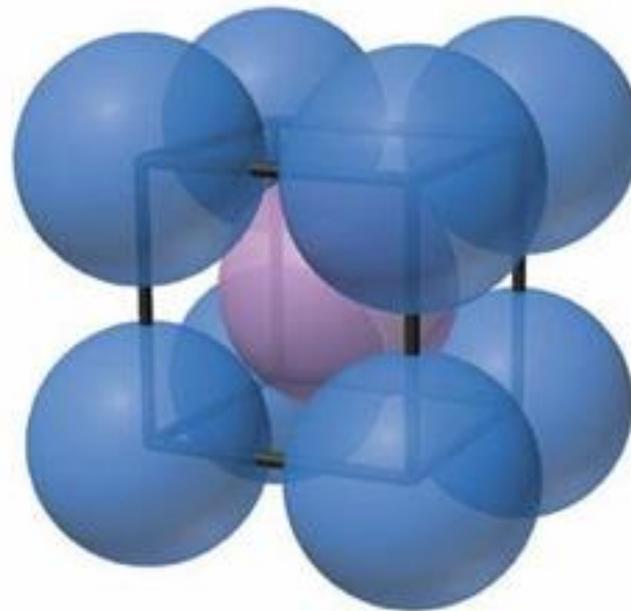
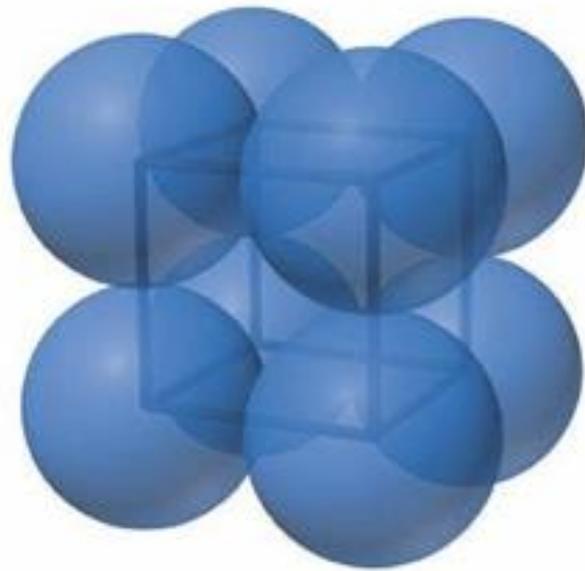
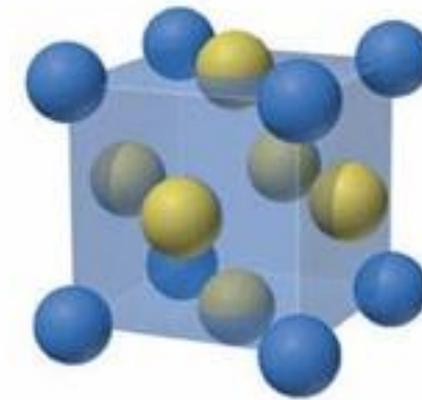
Simple cubic



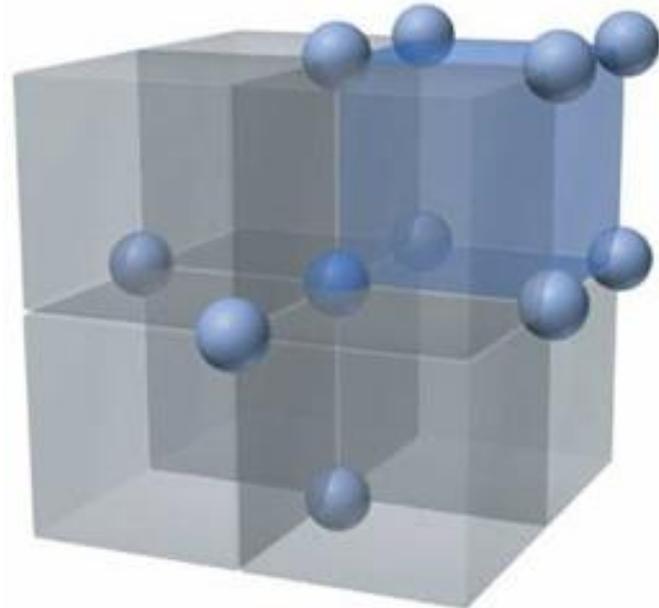
Body-centered cubic



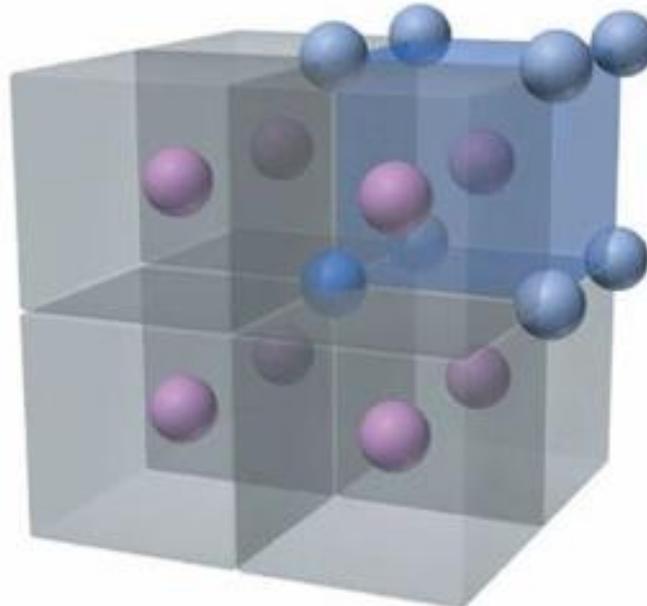
Face-centered cubic



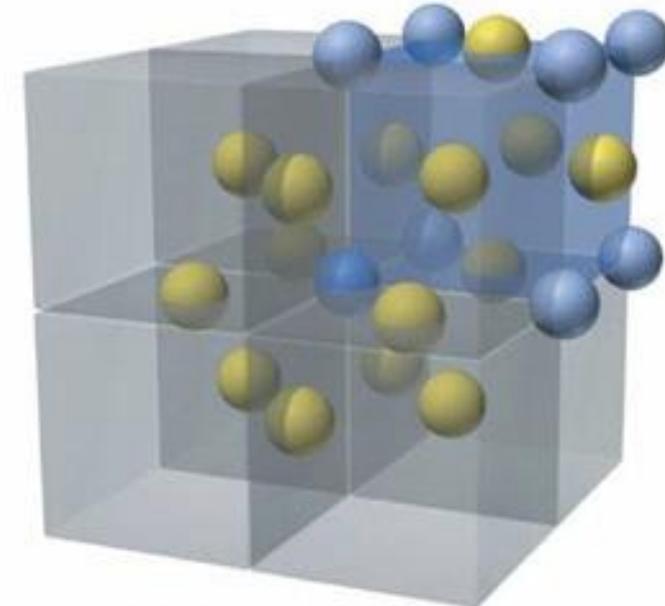
Posições iniciais



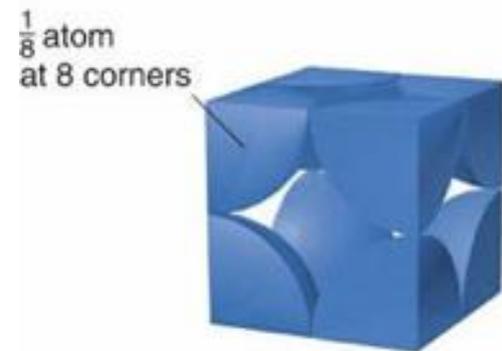
Coordination number = 6



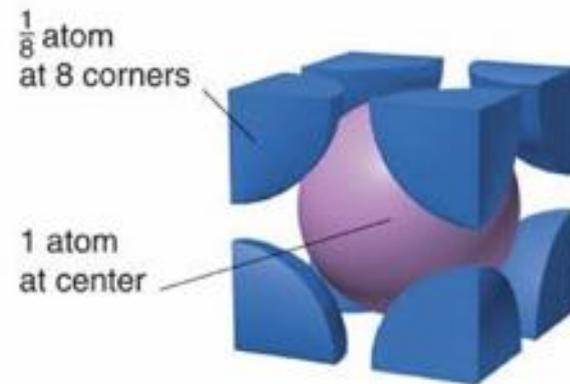
Coordination number = 8



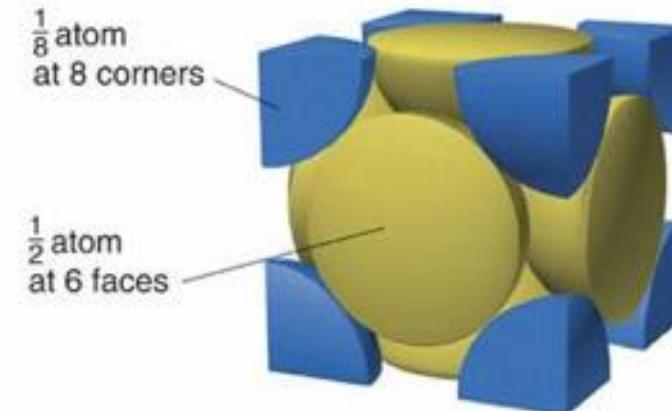
Coordination number = 12



Atoms/unit cell = $\frac{1}{8} \times 8 = 1$



Atoms/unit cell = $(\frac{1}{8} \times 8) + 1 = 2$



Atoms/unit cell = $(\frac{1}{8} \times 8) + (\frac{1}{2} \times 6) = 4$

Limitações da Dinâmica Molecular (III)

3) Limitações nas escalas de tempo e espaço

As limitações no tamanho da célula computacional de Dinâmica Molecular

Limitação do tempo de simulação

Limitações da Dinâmica Molecular (III)

3) Escala temporal

O passo **máximo** de integração em simulações de Dinâmica Molecular é definido pelo movimento mais rápido do sistema.

Frequências vibracionais em um sistema molecular são da ordem de 3000cm^{-1} (~10 femtosegundos)

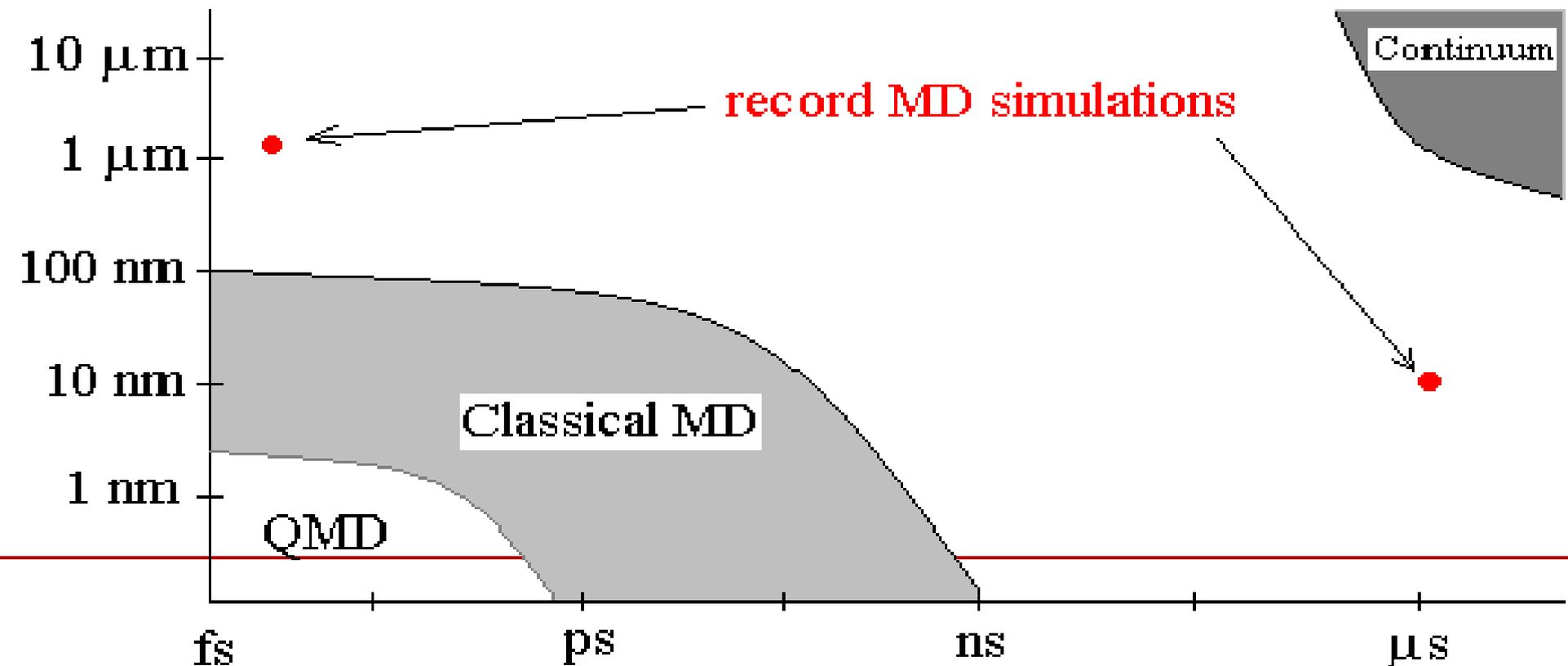
Frequências ópticas são da ordem de 10THz (período de 100fs)

Um típico passo de integração em Dinâmica Molecular é da ordem de **FEMTONSEGUNDOS** (10^{-15}s)

Length-scale:

The size of the computational cell is limited by the number of atoms that can be included in the simulation, typically $10^4 - 10^7$. This corresponds to the size of the computational cell on the order of **tens of nm**. Any structural features of interest and spatial correlation lengths in the simulation should be smaller than the size of the computational cell.

To make sure that the finite size of the computational cell does not introduce any artifacts into the simulation results, one can perform simulations for systems of different size and compare the measured properties.



Condições de contorno

A escala espacial em Dinâmica Molecular também é limitada:
Maior parte dos átomos que estão na superfície “sentem” a presença da superfície.

Como reproduzir as interações atômicas em uma célula computacional em Materiais ?

Condições de contorno (Livre)

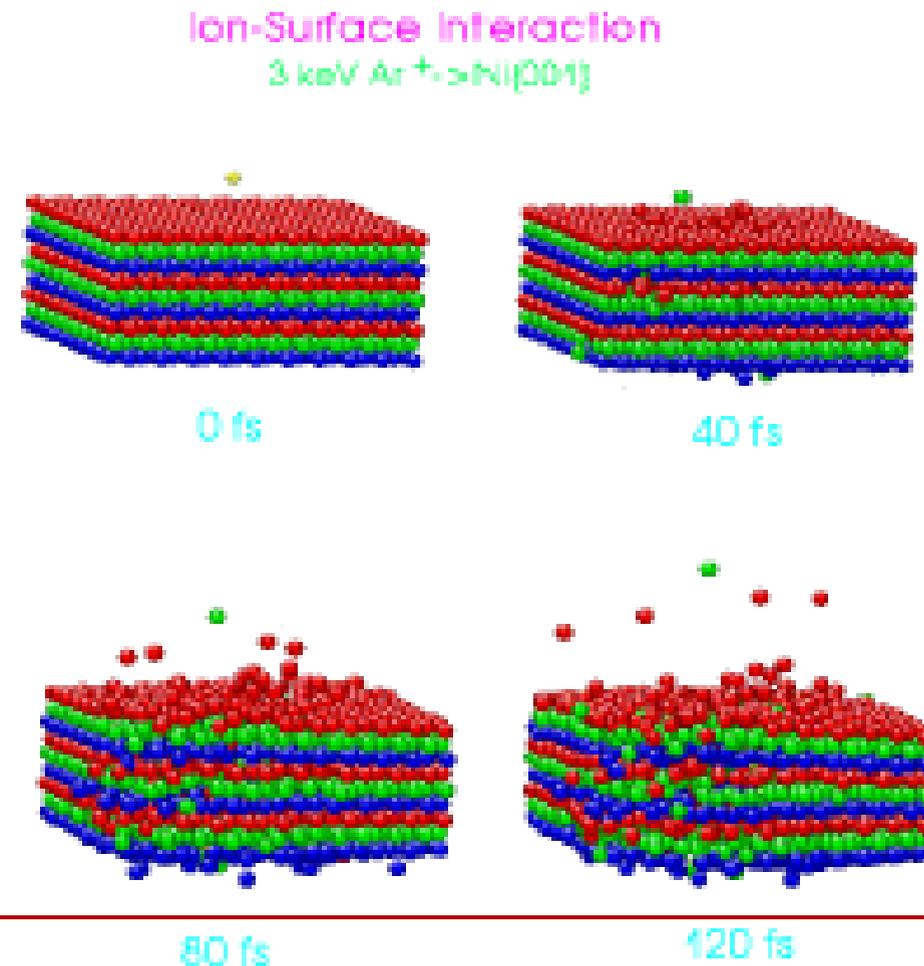
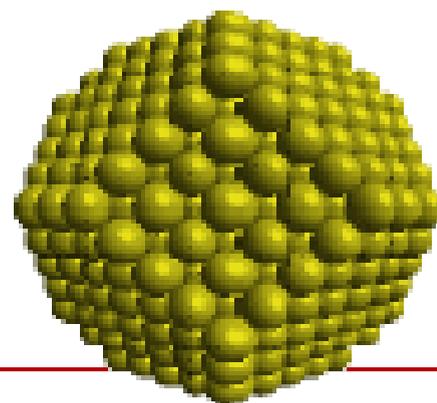
1. Free boundaries (or no boundaries). This works for a molecule, a cluster or an aerosol particle in vacuum. Free boundary condition can be also appropriate for ultrafast processes when the effect of boundaries is not important due to the short time-scale of the involved processes, e.g. fast ion/atom bombardment, etc.

MD

Examples of free boundary conditions in MD:

Ultrafast process of sputtering

Free cluster



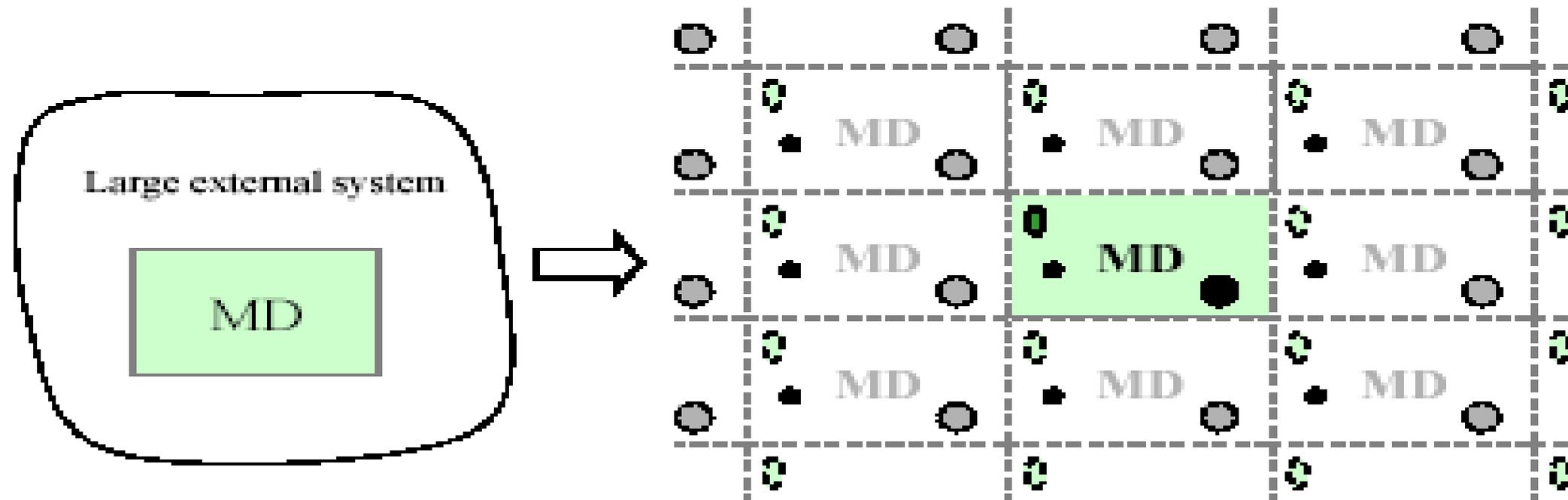
Condições de contorno - Rígidas

2. Rigid boundaries (atoms at the boundaries are fixed). In most cases the rigid boundaries are unphysical and can introduce artifacts into the simulation results. Sometimes used in combination with other conditions (stochastic and periodic conditions, as discussed below).



Condições de contorno periódicas

3. **Periodic boundary condition** (eliminates surfaces – the most popular choice of boundary conditions). This boundary conditions are used to simulate processes in a small part of a large system.



All atoms in the computational cell (green box) are replicated throughout the space to form an infinite lattice. That is, if atoms in the computational cell have positions \vec{r}_i , the periodic boundary condition also produces mirror images of the atoms at positions defined as

$$\vec{r}_i^{\text{image}} = \vec{r}_i + l\vec{a} + m\vec{b} + n\vec{c} \quad \text{where } \vec{a}, \vec{b}, \vec{c} \text{ are vectors that correspond to the edges of the box, } l, m, n \text{ are any integers from } -\infty \text{ to } +\infty.$$

Condições de contorno periódicas

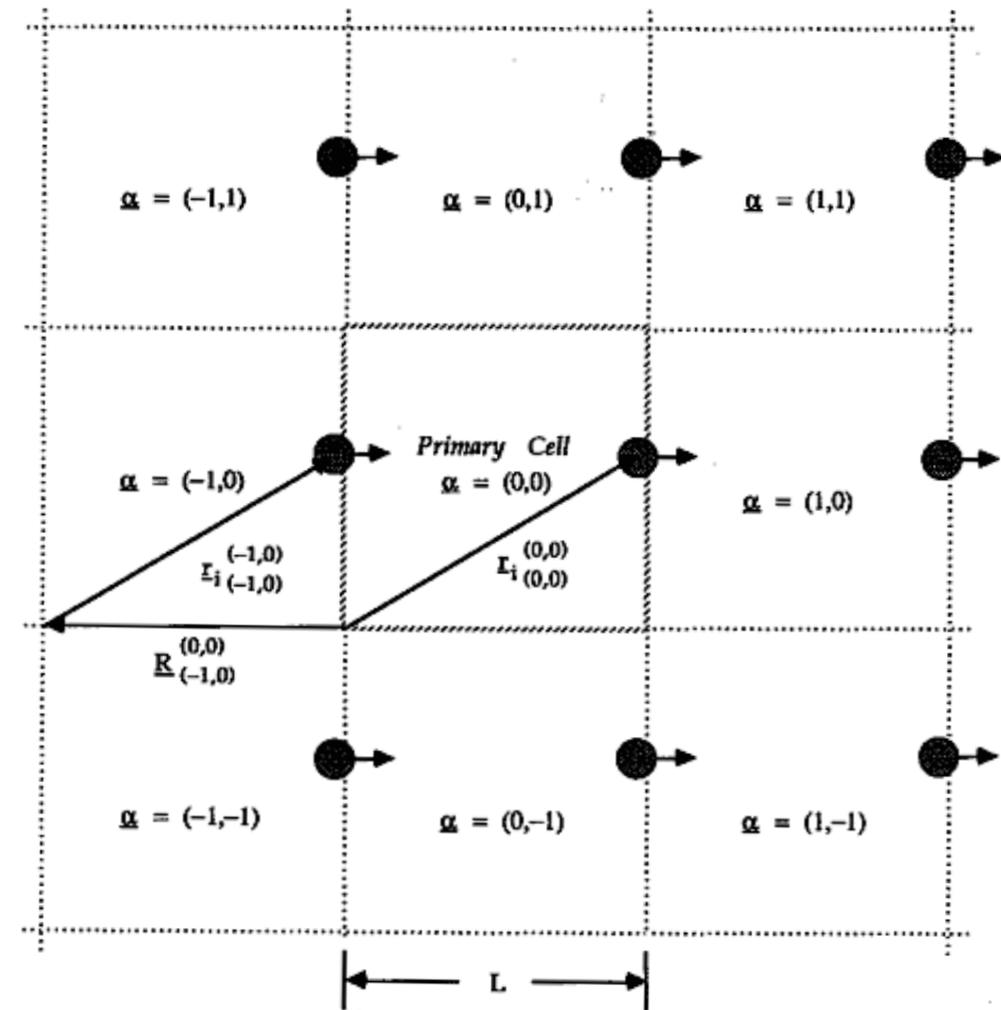
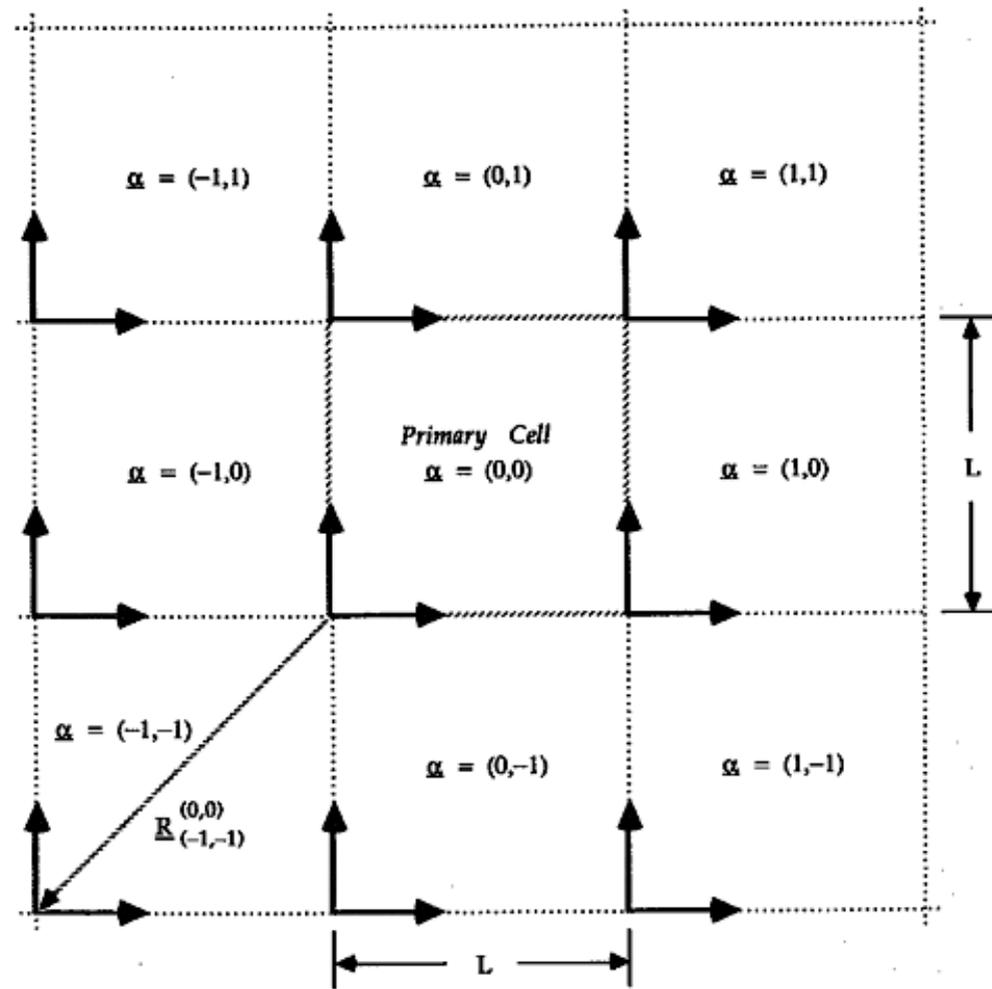
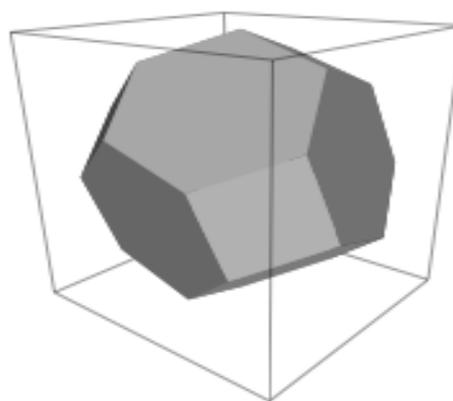
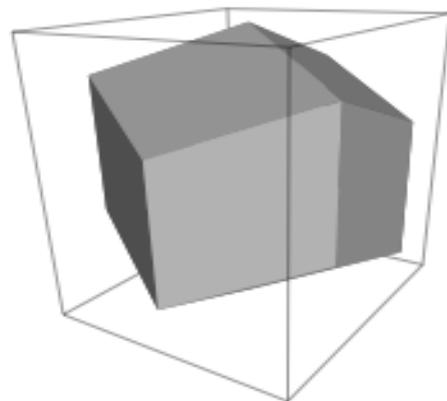


FIGURE 2.13 Periodic boundary conditions in two dimensions. The primary cell is surrounded by eight image cells and each cell is identified by a cell translation vector α . Each cell has a reference frame whose origin is the lower left corner of the cell. Each image frame is located wrt the primary frame by a vector \mathbf{R} , such as the one shown here for cell $\alpha = (-1, -1)$.

Condições de contorno periódicas

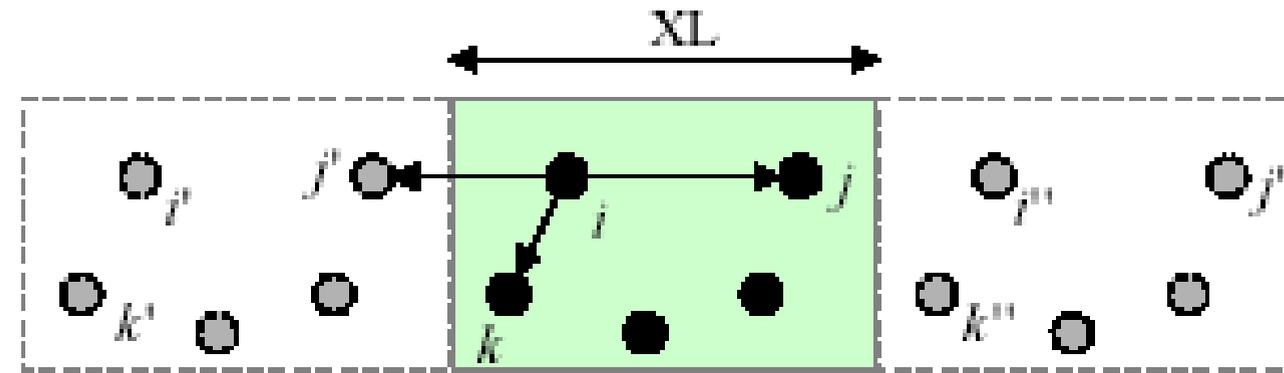


box type	image distance	box volume	box vectors			box vector angles		
			a	b	c	$\angle bc$	$\angle ac$	$\angle ab$
cubic	d	d^3	d 0 0	0 d 0	0 0 d	90°	90°	90°
rhombic dodecahedron	d	$\frac{1}{2}\sqrt{2}d^3$ $0.707d^3$	d 0 0	0 d 0	$\frac{1}{2}d$ $\frac{1}{2}d$ $\frac{1}{2}\sqrt{2}d$	60°	60°	90°
truncated octahedron	d	$\frac{4}{9}\sqrt{3}d^3$ $0.770d^3$	d 0 0	$\frac{1}{3}d$ $\frac{2}{3}\sqrt{2}d$ 0	$-\frac{1}{3}d$ $\frac{1}{3}\sqrt{2}d$ $\frac{1}{3}\sqrt{6}d$	71.53°	109.47°	71.53°

Condições de contorno periódicas

Calculation of distances between atoms with periodic boundary conditions:

When the minimum image criterion is satisfied, a particle can interact only with the closest image of any other particle.

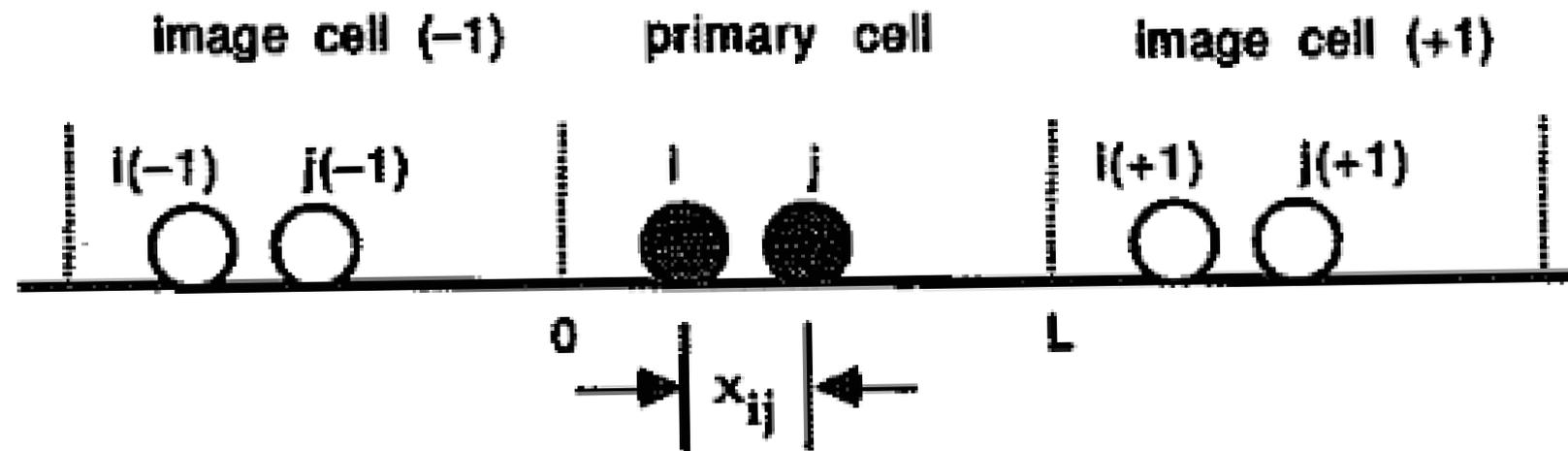


The closest image may or may not belong to the computational cell. Therefore, in the code, if a particle j is beyond the range of interaction with particle i ($R_{ij} > R_{cut}$), we have to check the closest images. For example, in MSE524-MD code, an algorithm for checking the closest image is:

```
IF(LIDX.EQ.1) THEN                                where  $DX = X_j - X_i$   
  IF(DX.GT.XLHALF)  $DX=DX-XL$                      $XLHALF = XL/2$   
  IF(DX.LT.-XLHALF)  $DX=DX+XL$   
ENDIF
```

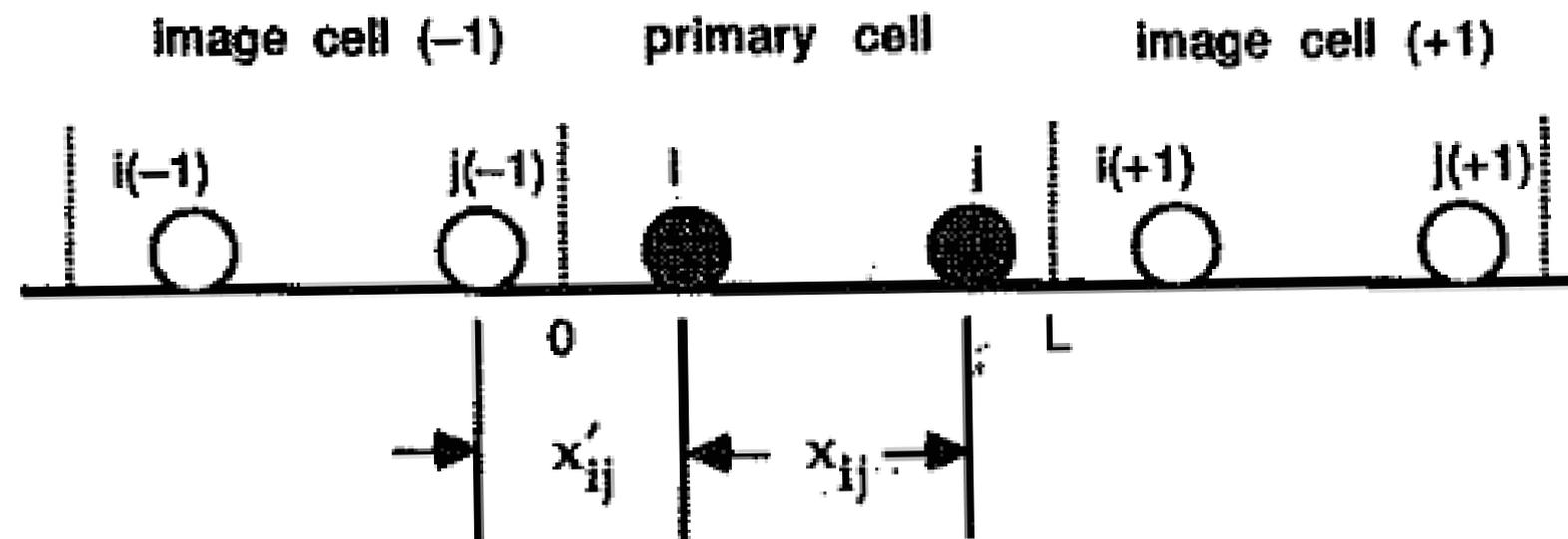
Critério da imagem mínima

Situation A: $x_{ij} < L/2$



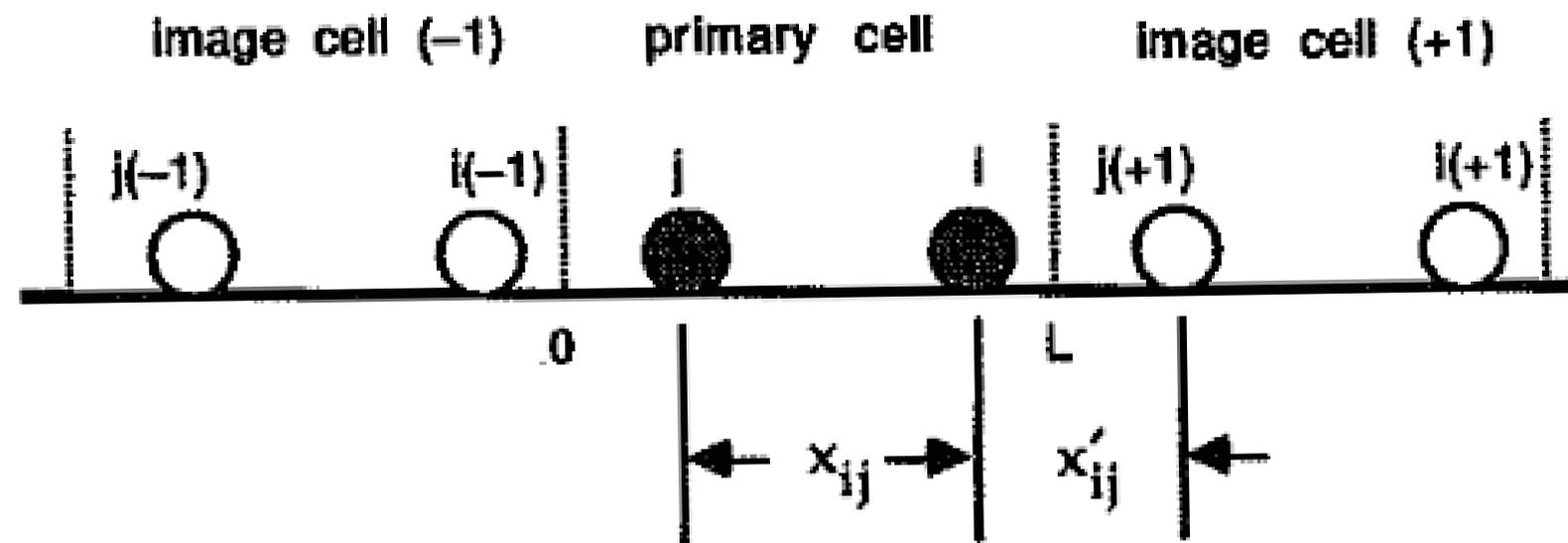
Critério da imagem mínima

Situation B: $x_{ij} < -L/2$ $x_{ij} \rightarrow x'_{ij} = x_{ij} + L$



Critério da imagem mínima

Situation C: $x_{ij} > L/2$ $x_{ij} \rightarrow x'_{ij} = x_{ij} - L$



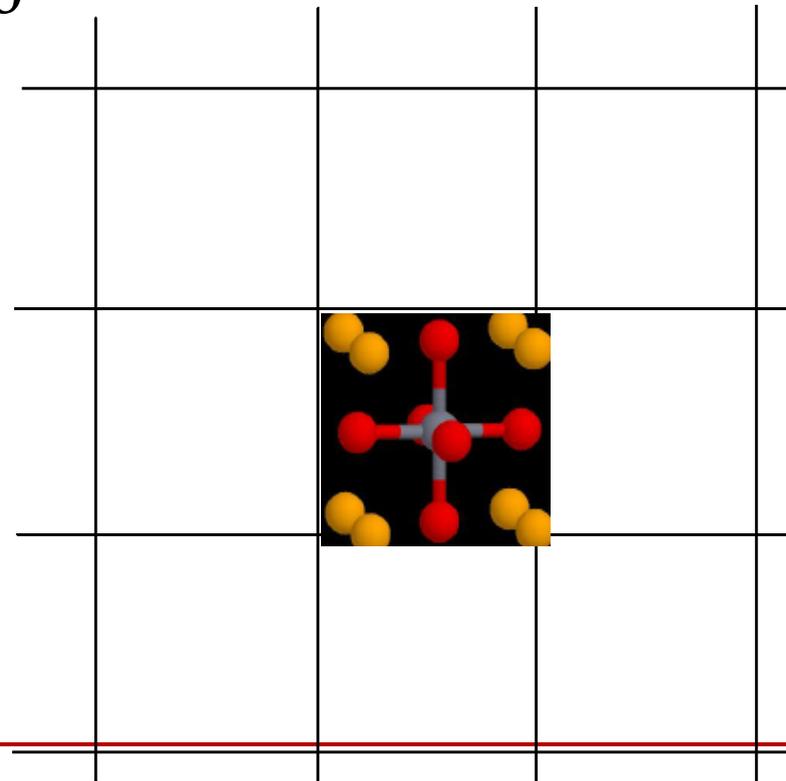
Tamanho do sistema e condições de contorno

Sistema finito (ex. molécula ou cluster)

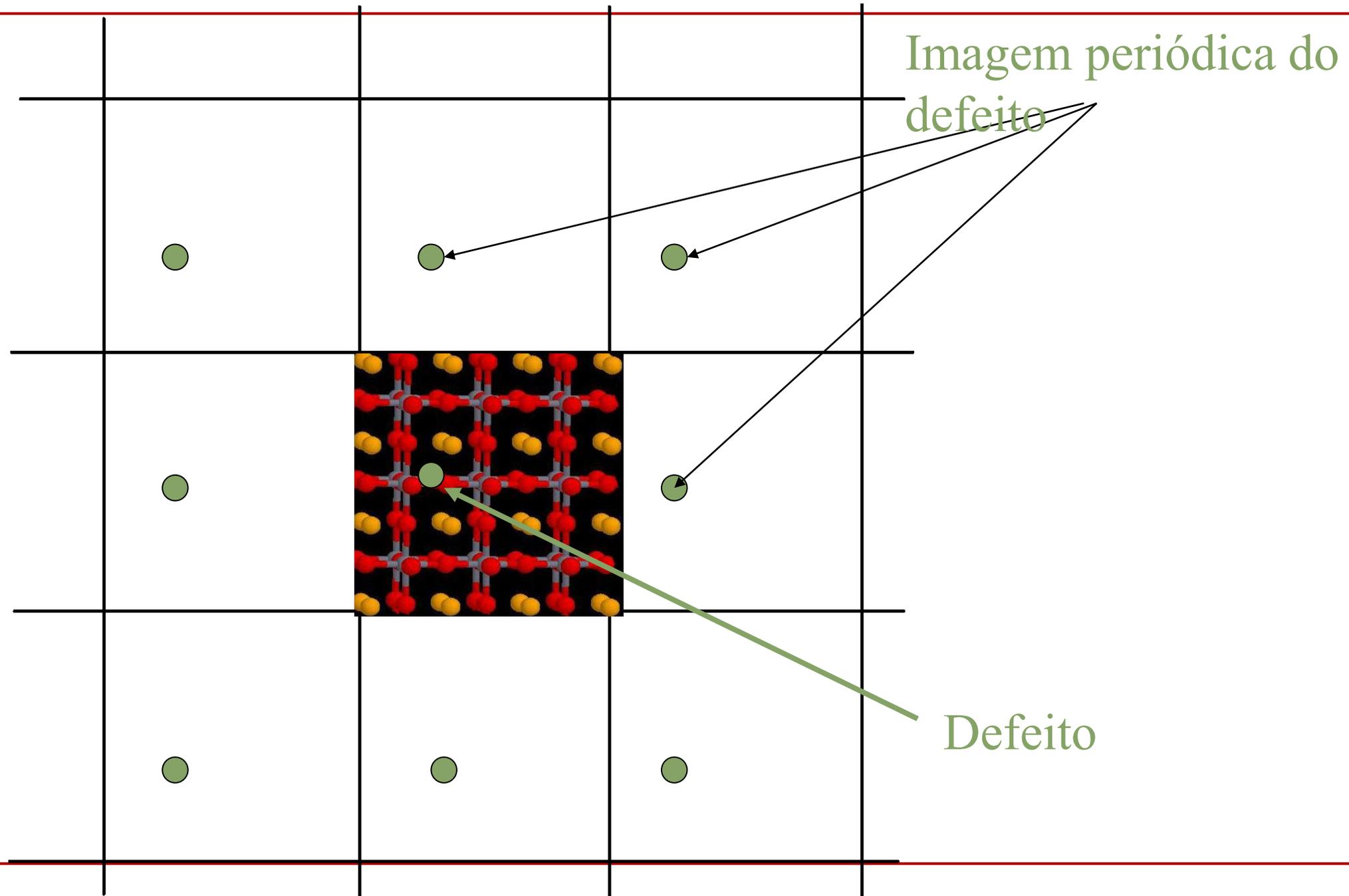
Sem problemas; -> simplesmente use todos os átomos

Sistema infinito (ex. sólidos/líquidos)

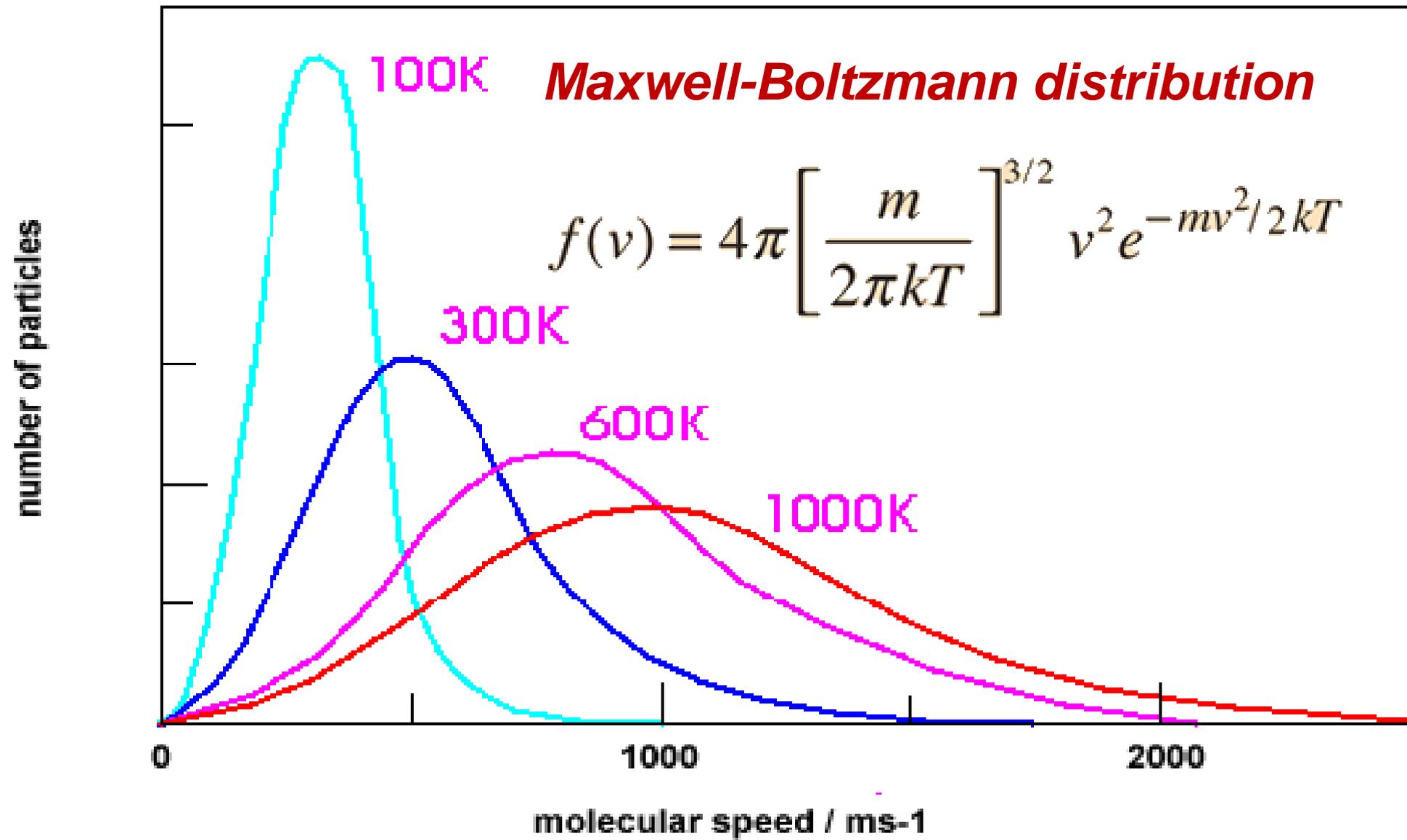
Não podemos aproximar como sistema finito -> uso das Condições Periódicas de Contorno



Como tratar defeitos ?



Velocidades iniciais



Schematic diagram of a basic MD code

